EQUILIBRIA IN CARBOXYLATE SOLUTIONS

by

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SUMMARY

A considerable number of physicochemical investigations indicate that self-association occurs in aqueous solutions of organic acids, but no precise studies of the equilibria present appear to have been conducted. Methods recently developed for identifying inorganic isopolyacid equilibria have been applied to several monocarboxylic acids at 25.00 $\pm$ 0.05°C. Potentiometric measurements were carried out on buffer solutions of phenylacetic, cyanoacetic, chloroacetic, glycollic, methoxyacetic, phenoxyacetic, and mandelic acids in a 3M sodium (perchlorate) ionic medium and over a wide range of total carboxylate concentration and of pH.

The pH of the carboxylate buffers in the constant ionic medium changed with increase in the total carboxylate concentration. This change has been ascribed to polynuclear complex formation and rigorous methods of mathematical analysis applied. The monomeric acid HA is the only species formed at low total carboxylate concentrations, A $\leq$ 50mM, but at higher concentrations the results are consistent with the formation of the species HA_2^- and H_2A_2. In the mandelate system the higher species $H_2A_3^-$ and H_3A_3 are also detectable. All the species have been characterised by their formation constants, and the values are discussed with reference to the probable structure of the complexes and the nature of the carboxylate ions. The association is assumed to occur by hydrogen bonding, with alternate additions of monocarboxylate ions and protons. The evidence suggests that the dimer exists in the extended form with only one hydrogen bond rather than in the cyclic form.

There is also evidence showing that copper(II) acetate and its higher homologues exist as dimers in the crystalline state, in certain organic solvents, and possibly in water. Since the method of competitive complex formation between protons and copper(II) ions for the carboxylate ions was used to study the copper(II) carboxylate equilibria, a necessary preliminary was the above investigation of the analogous proton carboxylate equilibria. Experimental conditions similar to those used in the acid systems were employed to make a precise study of the copper(II) carboxylates and to establish which species exist in aqueous solution. For copper(II) concentrations between 10mM and 100mM, and free carboxylate concentrations up to about 540mM neither polynuclear complexes nor mixed complexes of the type $CuHA_2$ were detectable. All the experimental results are explicable in terms of the stepwise equilibria

$$Cu^{2+} + nA^{-} \rightleftharpoons CuA_n^{(2-n)+} \qquad \text{where } n \leq 3.$$

The parallelism between the stability of the proton and the copper(II) carboxylates is discussed and the high stability constants of the glycollate, mandelate, methoxyacetate, and phenoxyacetate complexes is ascribed to chelation.

List of Symbols

A	Total carboxylate ion concentration
A_1	Concentration of carboxylate ion present as mononuclear species
A_{poly}	Concentration of carboxylate ion present as polynuclear species
a	Free carboxylate ion concentration
B	Total metal ion concentration
b	Free metal ion concentration
C_A	Concentration of sodium carboxylate
C_B	Concentration of base
C_H	Concentration of perchloric acid
C'_H	Concentration of perchloric acid remaining when E_o titration is stopped
C_{HA}	Concentration of carboxylic acid
E	Measured potential
E_j	Liquid junction potential
E_o	Standard potential of glass electrode
H	Total hydrogen ion concentration
h	Free hydrogen ion concentration
h_{Cu}	Concentration of perchloric acid in copper perchlorate solution
K_D	Stability constant for $2HA = H_2A_2$
K_{DT}	Stability constant for $H_2A_2 + HA = H_3A_3$
K_T	Stability constant for $3HA = H_3A_3$
K_{pq}	Step stability constant for formation of H_pA_q from either $H_{p-1}A_q$ or H_pA_{q-1}
K'_{23}	Stability constant for $HA_2 + HA = H_2A_3$

K_n	Stability constant for $BA_{n-1} + A \rightleftharpoons BA_n$
M	Molar
mM	Millimolar (millimoles)
n,p,q	Integers
N,P,Q	Integers - maximum values of n,p,q
$\bar{n}$	Average number of ligands bound per central group
$\bar{n}_c$	Value of $\bar{n}$ at isohydric point
$\bar{n}_H$	Average number of hydrogen ions bound per carboxylate group
$\bar{n}_l$	Average number of ligands bound per central group in mononuclear species
$\bar{n}_{poly}$	Average number of ligands bound per central group in polynuclear species
$\bar{p}$	Average number of ligands per complex
$\bar{q}$	Average number of central groups per complex
$\bar{p}_{poly}$	Average number of ligands per polynuclear complex
$\bar{q}_{poly}$	Average number of central groups per polynuclear complex
$\bar{r}$	Reciprocal of the average degree of condensation
$\bar{r}_{poly}$	Reciprocal of the average degree of condensation in polynuclear species
pH	$-\log_{10}$(free hydrogen ion concentration)
p*,v	Parameters
V_A	Volume of perchloric acid
V_B	Volume of base
V_e	Volume of base added at end point
V_i	Initial volume in titration vessel
V_T	Total volume in titration vessel

A^*, a^*, h^*	Normalised functions
α_c	Fraction of total central group in form of species BA_c
α_{pq}	Fraction of A in form of species H_pA_q
β_n	Overall stability constant of species BA_n
β_{pq}	Overall stability constant of species H_pA_q
γ_H	Activity coefficient of hydrogen ions

C H A P T E R 1.

INTRODUCTION.

1 - A. COMPLEXES.

The increased study of complexes in solution during the past two decades constitutes a major part of the resurgence of interest in physico-inorganic chemistry. A complex can most simply be defined as the result of reversible association in solution of two species A and B to form a third species B_qA_p, $q \geq 1$, $p \geq 0$. The discovery of the first complex is usually attributed to Tassaert (1798) who observed that cobalt salts combine with ammonia. More recently, however, the emphasis has shifted from isolating and identifying coordination compounds, to the identification and determination of the thermodynamic stability of the several species which usually co-exist in solution. The formulation of the law of mass action by Guldberg and Waage was the initial step in the quantitative study of chemical equilibria.

At the turn of the century it was recognised that complex formation is a stepwise process and the early work in this field has been reviewed by Sillén(1958), Tobias(1958), and, in greater detail, by Rossotti and Rossotti(1961a). After this early beginning, progress in the study of ionic equilibria slowed greatly during the 1920's and 1930's. However, the publication of Bjerrum's(1941) and Leden's(1941) methods for computing step

stability constants was the impulse from which the present widespread investigations have arisen. Work described in this thesis is on the various equilibria present in aqueous carboxylate solutions with, and without, copper(II) ions present.

1 - B. BASIC PRINCIPLES.

The stepwise nature of mononuclear complex formation became generally accepted through the work of the Bjerrums(1921;1941). The various species present in solution are considered to arise from the series of reactions

$$BA_{n-1} + A \rightleftharpoons BA_n \qquad (1\text{-}1)$$

between the metal ions B and ligands A, where $0 < n \leq N$, and N is the maximum number of ligands which coordinate. Here and elsewhere charges have been omitted for clarity. The concentration of the species BA_n is related to the concentrations of A and BA_{n-1} by the step stoichiometric stability constant, K_n, which is given by

$$K_n = [BA_n]/[BA_{n-1}]a \qquad (1\text{-}2)$$

where a is the concentration of free ligand. The overall stoichiometric stability constant, β_n, for the reaction

$$B + nA \rightleftharpoons BA_n \qquad (1\text{-}3)$$

is given by

$$\beta_n = [BA_n]/ba^n \qquad (1\text{-}4)$$

where b is the concentration of free central group.

Thus $\beta_o = K_o = 1$; $\beta_1 = K_1$; and $\beta_n = \prod^{n} K_n$. (1-5)

Stoichiometric stability constants are thermodynamic stability constants which are valid for a standard state defined by the detailed composition of the solution. In the present studies the activity coefficients have been held effectively constant by the use of a 3M sodium ionic medium at 25°C. [See also Sec 1-E]

The secondary concentration variables which Bjerrum(1915,1921) introduced are very helpful in the computation of stability constants. These quantities, designated by $\bar{n}$ and α_c, are the average number of ligands bound to each central group, and the fraction of total central group in the form of the complex BA_c, respectively.

For a system of mononuclear complexes the total concentrations, A and B, of the ligand and central group respectively, are given by

$$A = a + [BA] + 2[BA_2] + \ldots\ldots\ldots + N[BA_N] = a + b\sum_{0}^{N} n\beta_n a^n \qquad (1\text{-}6)$$

and

$$B = b + [BA] + [BA_2] + \ldots\ldots\ldots + [BA_N] = b\sum_{0}^{N} \beta_n a^n \qquad (1\text{-}7)$$

Combining Eqs (1-6) and (1-7), we have

$$\bar{n} = (A-a)/B = \sum_{0}^{N} n\beta_n a^n \Big/ \sum_{0}^{N} \beta_n a^n \qquad (1\text{-}8)$$

and

$$\alpha_c = [BA_c]/B = \beta_c a^c \Big/ \sum_{0}^{N} \beta_n a^n \qquad (1\text{-}9)$$

The plot of $\bar{n}$ against log a is called the formation curve. This is the form into which the experimental data in the present studies are converted, before evaluating the stability constants.

Equations (1-8) and (1-9) show that $\bar{n}$ and α_c are functions

of a only, provided that the system is entirely mononuclear. However, if polynuclear species are formed these quantities also depend on the total concentration of B. In systems containing polynuclear species, B_qA_p, the overall stoichiometric stability constant for the equilibrium

$$qB + pA \rightleftharpoons B_qA_p \tag{1-10}$$

is given by

$$\beta_{qp} = [B_qA_p]/b^qa^p \tag{1-11}$$

Thus the total concentrations of ligand and central group, respectively, are given by

$$B = \sum_{1}^{Q} \sum_{0}^{P} q\beta_{qp}b^qa^p \tag{1-12}$$

and

$$A = a + \sum_{1}^{Q} \sum_{1}^{P} p\beta_{qp}b^qa^p \tag{1-13}$$

Combination of Eqs. (1-12) and (1-13) gives

$$n = \frac{A-a}{B} = \frac{\sum_{1}^{Q} \sum_{1}^{P} p\beta_{qp}b^qa^p}{\sum_{1}^{Q} \sum_{0}^{P} q\beta_{qp}b^qa^p} \tag{1-14}$$

For systems in which q is not a variable, but has a unique value, $\bar{n}$ will again be a function of a only. These systems are termed "homonuclear".

In carboxylic acid systems the species HA, HA_2, H_2A_2,.., H_pA_q

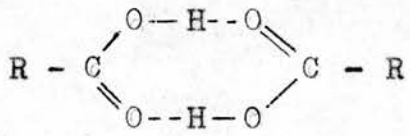
(where HA is the monomeric acid and p and q are integers) may occur in addition to carboxylate ions, A, and protons. When investigating these the carboxylate ion has been considered as the central group, and the protons as ligands. Hence $\bar{n}$ is defined as the average number of protons per carboxylate group. In instances where confusion may arise between the two senses in which $\bar{n}$ is used, this latter quantity is designated by $\bar{n}_H$. [e.g. in Sec. 3 - G]

1 - C. ASSOCIATION OF CARBOXYLIC ACIDS.

This series of studies has been concerned, in part, with the identification of the species present in aqueous solutions of phenylacetic, cyanoacetic, chloroacetic, methoxyacetic, phenoxyacetic, glycollic, and mandelic acids, and the determination of their stability constants. In this short review on the association of carboxylic acids particular attention is paid, therefore, to previous work on aqueous solutions.

Results from a variety of measurements on carboxylic acids in the vapour phase, or dissolved in non-polar solvents, have shown that self-association occurs. Although the first reliable measurements of the association in the vapour phase were those of Ramsay and Young(1886), investigations in this field date back to the work of Bineau(1846). Vapour density and spectroscopic methods, in the most part, have been used in such investigations.

Formic and acetic acids have been most widely studied, but measurements on other acids have given similar results. The general conclusion is that organic acids exist as dimers, in the vapour phase, resulting from hydrogen bonding between the carboxyl groups. These dimers have the planar ring configuration I.



I

A much wider variety of methods have been used to investigate association in organic solvents, and conclusions similar to the above have been reached. Much of the work on solutions of carboxylic acids in aprotic solvents has been directed towards the determination of the equilibrium constant K_D, for the reaction

$$2HA \rightleftharpoons H_2A_2 \qquad (1\text{-}15)$$

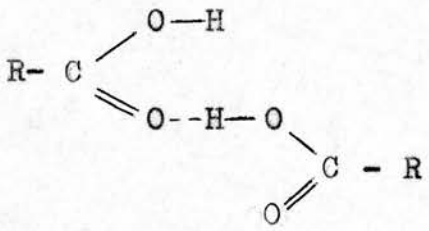
This quantitative aspect, as well as the historical background, and qualitative investigations have been reviewed by Allen and Caldin(1953), and more recently by Pimentel and M^{c}Clellan(1960).

Studies on the association of acids in the liquid phase have also been largely confined to formic and acetic acids. The conclusions are that polymerisation takes place at least in formic acid, and probably in acetic acid, but the latter is to a great extent dimeric. Martin(1961), has reviewed such work as has been done in this field.

Crystal structures of a wide selection of monocarboxylic acids have been determined. Formic acid (Holtzberg et al. 1953), and

acetic acid (Jones and Templeton 1958), have been shown to exist as infinite chains, with successive molecules connected by single hydrogen bonds. Crystalline benzoic (Sim et al. 1955), β-nitropropionic (Sutor et al. 1954), phenyl-propiolic (Rollet 1955), and long chain fatty acids (Sydow 1955, 1956; Abrahamsson 1959), on the other hand, assume the cyclic dimer structure. X-ray diffraction measurements by Weiss(1959), on chloroacetic acid, and nuclear magnetic resonance studies by Goldman(1958), and Yagi and Ueta(1959), on crystalline trichloroacetic acid have indicated that these acids have a dimeric structure, but no configuration has been suggested.

Barceló and coworkers(1958) studied the infrared spectra of the crystalline α and β polymorphs of chloroacetic acid and inferred that the former consists of cyclic dimers, while the latter, it was tentatively suggested, has an open structure II. Nakamura(1959),

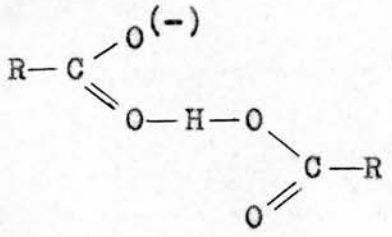


II

also using infrared spectra, arrived at the opposite conclusion. He assigned the structure I to the β and ϒ polymorphs, and a polymeric structure, similar to that found in formic and acetic acids, to the α form.

Salts of the type MHA_2, where M is a univalent cation, have

been extensively studied by diffraction methods. Speakman(1948,1949) using X-ray diffraction, and Bacon and Curry(1957) using neutron diffraction concluded that the ion HA_2 was the main structural unit of potassium hydrogen bisphenylacetate. The ion HA_2 has the configuration III with an, at least statistically, symmetrical



III

hydrogen bond. Davies and Thomas(1951), on the other hand, inferred from infrared absorption spectra that normal carboxyl and carboxylate ion groups were present in this salt, but in the light of the other work their interpretation is doubtful. The Glasgow school has identified the structural unit HA_2 in the crystals of the acid salts of p-hydroxybenzoic(Skinner and Speakman 1951), benzoic (Skinner et al.1954), acetic(Speakman 1959a; Speakman and Mills 1961), o-nitrobenzoic(Shrivastava and Speakman 1961), anisic, cinnamic, and glycollic(Speakman 1959b) acids, but not in salicyclic(Downie and Speakman 1954) or p-nitrobenzoic(Shrivastava and Speakman 1961) acids where the two carboxylate residues are crystallographically distinct. A neutron diffraction determination of the structure of potassium hydrogen maleate by Peterson and Levy(1958) showed that a hydrogen bond, similar to that in the HA_2 ions, was present between the two

carboxylate residues in the maleate ion.

Molecular association of carboxylic acids in aqueous solution has aroused much less interest than association in organic solvents. To a large degree, this can be ascribed to the assumption that the high dielectric constant of water, and solvation of the acid molecules, so decrease the tendency to dimerise as to make associated species undetectable. While this is undoubtedly the case in very dilute solutions, such an assumption is unjustified where more concentrated solutions ($\gtrsim$0.05M) are concerned.

Abegg (1894) observed that the molecular depressions of the freezing point of concentrated aqueous solutions of acetic and propionic acids decreased as the concentration of acid increased. Since then evidence has gradually accumulated to support the view that dimeric species, and to a lesser extent polymeric species, are present in aqueous solution. At the turn of the century the cryoscopic method was the most widely used means of studying association, and was employed by Roth(1903) who made measurements on acetic acid solutions up to 6.5% acetic acid. Unexpectedly small depressions were recorded and accounted for by self-association. Goebel(1912) derived an expression for calculating the self-association constants of solutes in aqueous solution, and obtained a value for K_D for acetic acid using data from Roth(1903) and Loomis(1897). Just before this the first quantitative determinations were reported by Peddle and Turner(1911) who used ebullioscopic and cryoscopic results to determine the degrees of self-association of a number

of organic acids. Further freezing point determinations have been performed by Jones and Bury(1927).

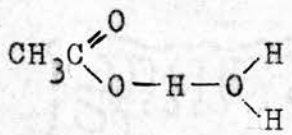
Vapour pressure measurements (MacDougall and Blumer 1933) and conductivity measurements have subsequently been used in attempts to assess K_D for the association of acids in water. The conductivity results of Saxton and Darken(1940) were used by Katchalsky and coworkers(1951) who considered that the concentration dependence of the ionisation constants indicated dimerisation. In deriving an expression for obtaining K_D they assumed that H_2A_2 has a cyclic structure and hence, contrary to the suggestion of Kolthoff and Bosch(1932), a negligible degree of dissociation. Thereafter they calculated K_D for eight monobasic acids. The validity of some of their assumptions has been questioned, however, by Davies and Griffiths(1954) who have carefully computed K_D from freezing point and distribution data.

Further consideration was given to conductivity data for aqueous solutions of formic, acetic, propionic, and butyric acids by Cartwright and Monk(1955), whose values of K_D are of the same order of magnitude as those of Davies and Griffiths. Substantiation of the order of these values has been derived from e.m.f. measurements (Nash and Monk 1957).

Density measurements have been applied to the investigation of micelle formation in concentrated butyric acid solution (Grindley and Bury 1929). The conclusion that butyric acid aggregates to form micelles in solutions containing $\geq$13% of the acid has been strengthened by specific heat measurements (Bury and Davies 1932).

Recalculation of Bury's data by Davies and Griffiths (1956) and Rossotti and Rossotti (1961b) has shown that $1 \leq q \leq \infty$ where q is the extent of association. Further evidence has come from ultrasonic measurements (White et al. 1958), and the solubility of the dye p-dimethylaminoazobenzene in solutions of butyric acid (Moule and Benson 1959), that micelles are formed in concentrated solutions.

Raman spectra have featured in this field during the last fifteen years in efforts to assign a configuration to the dimer H_2A_2. Traynard (1947) interpreted his observations as showing that the cyclic dimer was gradually replaced by hydrated monomeric molecules, of the form IV, when acetic acid was diluted with water.



IV

Batuev (1948), on the other hand, suggested that the solvent-solute complex was polymeric. The spectrum of liquid acetic acid was interpreted by Fénéant (1952a, 1952b) as showing that an equilibrium existed between the two forms of the dimer, I and II, while the spectra of aqueous solutions of various concentrations appeared to indicate that acetic acid forms at first open dimers of acetic acid monohydrate, and on raising the temperature, dihydrated monomeric molecules.

Further investigations by Cucurezeanu (1957a, 1957b, 1958) support Fénéant's conclusions; the open hydrated form of the dimer

being postulated as the predominant type. Even in equimolar solutions only small amounts of the cyclic form are said to be present. This interpretation has been substantiated by the density and viscosity of the solutions which reach a maximum at equimolar concentrations. That the open form of the dimer is predominant has also been shown by the enthalpy titrations of Martin (1961) [See also Martin and Rossotti(1961)].

While all the previous evidence pertains to the presence of the dimer H_2A_2 in aqueous solution, several mentions of the occurrence of the dimeric ion HA_2 appear in the literature. Dawson and Spivey (1930) investigated the catalytic influence of acetic acid and acetate buffers on the acetone-iodine reaction. They found that the equation relating the velocity of the reaction to the concentrations of the species present, required a term k[HA]a when acetate buffers were used. The results were therefore explained by postulating that the complex ion HA_2 was present, being formed by combination of the simple carboxylate ion with the undissociated acid. Bell and Jones (1953) extended the investigations to glycollate and trimethylacetate buffers as well as acetate buffers, and confirmed the previous conclusions. [See also Rossotti(1960a)].

When determining the solubility of benzoic acid in sodium benzoate solutions, Kolthoff and Bosch (1932) identified the hydrogen dibenzoate ion. From a consideration of the relative concentrations of hydrogen, benzoate, and complex ions, they suggested that dimeric benzoic acid is a much stronger acid than the monomer. It has

been suggested (Smith and Speakman 1948) that the exceptional solubility of phenylacetic acid in solutions of potassium phenylacetate is due to the formation of ions or micelles having the formula $[A^-(HA)_n]_m$. The acid salt, sodium dihydrogen trisphenylacetate has been shown (Smith 1953) to separate from incongruently saturated solutions, and another acid salt, possibly disodium hydrogen trisphenylacetate, probably exists in solution, but this was not confirmed.

1 - D. COPPER CARBOXYLATES.

The widespread growth of interest in inorganic chemistry is reflected in the not inconsiderable number of determinations of the stability of copper(II) carboxylates, which have been made, especially during the last fifteen years (Bjerrum *et al.* 1957). Most of the available experimental methods have been employed by the numerous investigators. Further, the calculations of the stability constants have been based on the assumption that only mononuclear species are formed in solution. Although the majority of values refer to the formation of cationic and neutral complexes of copper and other metals, there is a considerable number of constants relating to anionic complexes.

The realisation that the copper(II) salts of carboxylic acids are different from other copper(II) salts is of almost seventy years standing. Ewan(1894) attributed the difference between the absorption spectra of copper acetate and copper halides and sulphate

to the incomplete electrolytic dissociation of the former, and to the ion CuA having an absorption spectrum differing from that of the copper(II) ion. Sidgwick and Tizard (1908, 1910) studied the colour of copper(II) formate, acetate, propionate, and chloroacetate, and discovered that as the concentration was increased the depth of colour also increased, the more sharply the weaker the acid. It was suggested that below about 0.25molal, the point where a distinct greenish tinge made further measurements impossible, the solution contained only the molecule CuA_2 and the ions CuA, Cu, and A. The change in colour on dilution was considered to be due to the production of the ions at the expense of the undissociated molecule.

Absorption spectra have been used more recently as evidence supporting the assertion that the majority of copper(II) alkanoates have a binuclear structure. It has been shown that this is so in crystalline copper(II) acetate monohydrate by the X-ray diffraction structure of van Niekerk and Schoening (1953). The crystals of copper(II) formate tetrahydrate, on the other hand, have been shown (Kiriyama et al. 1954) to contain no such closely connected copper atoms.

Tsuchida and Yamada(1955) (Yamada et al. 1957) examined the visible and near ultraviolet absorption spectra of these two compounds, and of copper(II) propionate monohydrate, both in the crystalline state and in organic solvents. A band at 3750Å, in addition to the well known copper band at 7000 Å was observed in the spectra of crystalline copper(II) acetate and propionate, but

not in that of copper(II) formate. The former band was assumed to indicate a dinuclear structure with copper-copper interaction.

Tsuchida et al. (1956) (Yamada et al. 1958) extended their studies to the higher homologues of acetic acid. They concluded that copper(II) butyrate, valerate, capronate, caprylate, palmitate, and stearate had a dinuclear structure, whether crystalline, hydrated or anhydrous, or dissolved in ethanol or chloroform. Further evidence from infrared and ultraviolet spectra was advanced in support of their conclusions. All the alkanoates studied, with the exception of the formate, showed a sharp absorption at 1600 cm^{-1} in the infrared, and copper(II) palmitate and stearate had ultraviolet absorption spectra closely similar to that of copper(II) acetate. Spectral investigations have subsequently been carried out on the three copper(II) chloroacetates (Tsuchida et al. 1958) and bromoacetates (Tsuchida and Yamada 1958) in the crystalline state, hydrated and anhydrous, and in dioxan solution. The copper(II) trichloroacetate system was identified as mononuclear but there was some doubt about the structure of the dichloroacetate tetrahydrate: the remainder were dinuclear.

Abe (1953) had proposed that the anomalous paramagnetic resonance absorption of copper(II) propionate was due to interaction between pairs of copper atoms. Similarly, just before the publication of the structure of copper acetate, Bleaney and Bowers (1952) had attributed its anomalous paramagnetic resonance spectrum to the coupling together of pairs of copper(II) ions by

exchange forces. They also suggested that the copper(II) ions were bonded to four oxygen atoms in a plane - exactly as found a year later.

The anomalously low values obtained for the magnetic moment of copper(II) acetate [references quoted in Figgis and Martin (1956)] have been ascribed by Figgis and Martin(1956) to the existence of very weak covalent copper-copper bonds. These are δ-bonds formed by the lateral overlap of $3d_{x^2-y^2}$ orbitals, and have an exchange energy of approximately 1 kcal. mole $^{-1}$. Ross(1959) has reconsidered the paramagnetic resonance absorption spectra of Bleaney and Bowers(1952) and Abe and Shimada(1953), and confirmed the existence of the δ-bond.

The Australian workers, after their careful appraisal of copper(II) acetate, extended their investigations to some higher homologues (Martin and Waterman 1957). Again it was noticed that the temperature variation of the susceptibility was irregular in that antiferromagnetic rather than Curie-law characteristics were observed. This behaviour was so similar to that of copper(II) acetate that it was concluded that all the salts had fundamentally the same structure. Copper(II) formate, however, had a magnetic moment at room temperature of ~1.6 B.M., which was intermediate between that of its higher homologues (1.38 B.M.) and the value of 1.9 B.M. observed for magnetically dilute copper(II) compounds. This depressed value for a mononuclear compound has been attributed to strong intermolecular exchange forces.

Martin and Whitley(1958) thereafter carried out magnetic, cryoscopic, spectroscopic, and conductivity measurements on dioxan, benzene, and aqueous solutions of copper(II) alkanoates. The low values observed previously for the magnetic moments, excluding that of copper(II) formate, persisted in benzene and dioxan solutions. Cryoscopic and spectroscopic evidence supported the conclusion that the dinuclear structure was preserved in these solvents. In water, on the other hand, magnetic moments of 1.90 ± 0.05 B.M. were observed. It was further demonstrated by the other techniques that the dinuclear structure was destroyed in aqueous solutions, with dissociation into ions. Similar results have been obtained by Kondo and Kubo(1958a), who determined the magnetic moment of copper(II) acetate and in water, dioxan, and ethanol.

Copper(II) formate was found to adopt a dinuclear configuration in dioxan solution. Further efforts were made (Martin and Waterman 1959a,1959b) to induce copper(II) formate to adopt the dinuclear structure, as judged by the magnetic criterion. These endeavours resulted in the preparation of four dinuclear monoamine (pyridine, α-, β-, and γ-picoline) copper(II) formates, and the dioxan derivative $Cu_2(HCO_2)_4,C_4H_8O_2$.

Kondo and Kubo(1958b) measured the magnetic susceptibilities of the three copper(II) chloroacetates, the copper(II) salts of glycine and α-alanine, and copper(II) lactate, phenylacetate, diphenylacetate, and α-naphthylacetate. The sub-normal magnetic

moment associated with the acetate-type dinuclear structure was observed with the chloroacetate, phenylacetate, diphenylacetate, and α-naphthylacetate, but a normal moment was found for the trichloroacetic acid, glycine, α-alanine, and lactic acid salts. An intermediate value was obtained for the magnetic moment of the copper(II) dichloroacetate. This is in agreement with the spectroscopic results of the Japanese workers, [See page 14]. The normal magnetic moments of the glycinate, α-alaninate, and lactate were attributed to formation of monomeric chelates rather than dimers.

Many workers have reported the colour of the compounds and their solutions. Where dinuclear structures have been inferred green, or blue-green colours were observed, whereas a blue colour was observed in cases where mononuclear structures appeared to be present. It seems, therefore, that this colour difference is indicative of the presence or absence of the dinuclear structure.

Although the evidence strongly suggests that only mononuclear species exist in aqueous solutions of copper(II) alkanoates, there have been a few reports of dimeric species being identified. Pedersen(1945) and Fronaeus(1948) deduced from spectrophotometric and potentiometric measurements that dinuclear species were present in concentrated solutions. Graddon(1959;1960) has identified dimers in chloroform from a distribution study of copper(II) propionate between chloroform and water. Since distribution between two solvents cannot occur without a species common to both solvents, dimeric copper(II) propionate must be present to some extent, however small, in the aqueous phase.

1 - E. THE PRESENT WORK.

It has been shown that:

a) no systematic study has been carried out on aqueous solutions of carboxylic acids in an attempt to show the simultaneous presence of several associated species, and to evaluate their stability constants;

b) there is some doubt as to whether dimeric copper(II) alkanoates are present in aqueous solution.

This work is an extension to substituted acids, of the investigations by Martin(1961) on the formate, acetate, propionate, and butyrate systems, which were carried out to obtain further evidence on the nature of aqueous solutions of copper(II) alkanoates. As only slight evidence had been found to suggest the presence of dimers the aim in this work was threefold:

a) to continue the search for the presence of dimeric copper(II) carboxylates in aqueous solution.

b) to carry out precise investigations of the proton-carboxylate equilibria in the absence of metal ions,

c) to investigate the relationship between the stabilities of copper(II) carboxylates and of the corresponding acids.

The experimental approach in the copper(II) studies was to

follow the competitive complex formation between protons and copper(II) ions for the carboxylate ions. This was done by measuring the free hydrogen ion concentration as a carboxylic acid-sodium carboxylate buffer was added to a solution of copper perchlorate. However, before the copper(II) systems could be investigated satisfactorily a thorough study of the proton-carboxylate equilibria in the absence of copper(II) ions was necessary. A potentiometric titration procedure, incorporating a glass electrode in conjunction with a high precision potentiometer, has been used to measure the change in potential during the titrations. [Sec 2 - D]

When studying systems of complexes in solution it is an advantage to keep the activity coefficients of the reacting species constant. Concentrations of these species, and not their activities, can then be used to calculate stoichiometric stability constants by applying the law of mass action. The elimination of the activity coefficient from the calculations provides a great simplification and is essential in dealing with complicated equilibria where several products, whose formulae cannot be taken for granted, are formed. The activity coefficients are controlled by using a supporting electrolyte, usually a 1:1 salt of an alkali metal, in large excess so that the ionic composition of the medium is kept as constant as possible. This method has been known since the beginning of the century and, during the last fifteen years, has been applied by the Swedish school. The historical background has been summarised, and the validity of the method investigated, by Biedermann and Sillén(1953). The background salt

should form either no complexes, or else only very weak complexes, with the reacting species, and should contribute little to the property being studied. Sodium perchlorate, which is known to form weak complexes with some metals (Bjerrum et al. 1958; Jones et al. 1961), was chosen as the supporting electrolyte. All measurements were carried out on solutions in which the equivalent metal ion concentration was maintained at 3.00M.

Although the species present can be identified from the data obtained, the varying degrees of solvation and attachment of ions of the supporting electrolyte cannot be distinguished. Thus the concentration [BA] represents the sum of all the possible species given by (Sillén 1958).

$$[BA] = \sum \sum \sum [BA(H_2O)_x(Na^+)_y(ClO_4^-)_z] \qquad (1\text{-}16)$$

In the present series of investigations the results are usually consistent with the formation of the dimeric species HA_2 and H_2A_2, in addition to the monomer HA, in carboxylic acid solutions. The various equilibria present, and appropiate stability constants, are

$$H + A \rightleftharpoons HA \qquad K_{11} \qquad (1\text{-}17)$$

$$HA + A \rightleftharpoons HA_2 \qquad K_{12} \qquad (1\text{-}18)$$

$$HA_2 + H \rightleftharpoons H_2A_2 \qquad K_{22} \qquad (1\text{-}19)$$

$$2HA \rightleftharpoons H_2A_2 \qquad K_D \qquad (1\text{-}15)$$

Charges have again been omitted for simplicity.
The corresponding overall stability constants are designated by β_{11}, β_{12} and β_{22}.

As trimeric species were detected in the mandelate system the constants β_{23} and β_{33} have to be introduced into the calculations. The probable step equilibria are

$$H_2A_2 + A \rightleftharpoons H_2A_3 \qquad K_{23} \qquad (1\text{-}20)$$

$$H_2A_3 + H \rightleftharpoons H_3A_3 \qquad K_{33} \qquad (1\text{-}21)$$

$$H_2A_2 + HA \rightleftharpoons H_3A_3 \qquad K_{DT} \qquad (1\text{-}21)$$

$$HA_2 + HA \rightleftharpoons H_2A_3 \qquad K'_{23} \qquad (1\text{-}23)$$

$$3HA \rightleftharpoons H_3A_3 \qquad K_T \qquad (1\text{-}24)$$

Only mononuclear species were identified in the copper systems. One or more of the equilibria

$$Cu + A \rightleftharpoons CuA \qquad K_1 \qquad (1\text{-}25)$$

$$CuA + A \rightleftharpoons CuA_2 \qquad K_2 \qquad (1\text{-}26)$$

$$CuA_2 + A \rightleftharpoons CuA_3 \qquad K_3 \qquad (1\text{-}27)$$

were shown to occur in each system.

CHAPTER 2.

EXPERIMENTAL.

2 - A. REAGENTS.

Whenever possible reagents of AnalaR grade were used, and were not purified further. The source, and purification of the other chemicals are given.

Water: Distilled water was passed through an "Elgastat" mixed-bed deioniser and effluent with a resistance of 6×10^6 ohms, or more, retained. Any traces of carbon dioxide were removed by boiling when necessary.

Nitrogen: Carbon dioxide was removed from British Oxygen Gases nitrogen by bubbling it through a 40% sodium hydroxide solution. The nitrogen was then passed through 3.00M sodium perchlorate to saturate it with water vapour.

Potassium argentocyanide: A sample prepared by Brown's(1934) method was used.

Silver perchlorate: Silver oxide was precipitated from a concentrated solution of silver nitrate by the addition of sodium hydroxide solution. The precipitate was washed by centrifugation until free from sodium ions (zinc uranyl acetate test). Dilute perchloric acid was then added until almost all the silver oxide was dissolved, the neutral solution filtered to remove traces of silver oxide, and diluted to give a 0.1-0.2N solution of silver perchlorate.

The solution of silver perchlorate was analysed by Volhard's method using potassium thiocyanate previously standarised against spectroscopically pure silver wire with ferric ammonium sulphate as indicator.

Sodium perchlorate: The reagent grade anhydrous product of G. F. Smith & Co. and the hydrated "low in chloride" product of B.D.H., were used. Both of those were found to be free from chloride, chlorate and iron(III) ions but required recrystallising; the former to remove a small amount of silica which appeared when a solution of the original material was left standing for about one week, and the latter because the original product gave a distinctly yellow solution.

The concentrated original solutions were filtered through a sintered glass crucible, to remove insoluble matter, and then boiled until, at approximately 139°C, a skin of sodium perchlorate was formed. The anhydrous material, which crystallised on cooling to 90°C, was filtered off and the process repeated until about 80% of the sodium perchlorate had been recovered. The third and fourth crops of crystals from the B.D.H. product gave a slightly yellow solution. This sodium perchlorate was recrystallised a second time, and the filtrate added to the parent solution. Most of the yellow colour was removed from the aqueous layer by ether extraction. Dissolved ether was removed by gentle heating and a further three crops of crystals obtained.

Stock solutions of sodium perchlorate which were about 5molal, were analysed by drying weighed portions at 120°C to constant weight.

Perchloric acid.

Solutions were largely prepared by diluting 60% perchloric acid. Standardisation was carried out by titrating potassium hydrogen carbonate at 90°C using methyl red as indicator. The 0.01M solution used for standardising the glass electrode was prepared by diluting any convenient solution on hand.

Potassium hydrogen carbonate

The solid was kept in a desiccator under an atmosphere of carbon dioxide, and was used as a standard for the perchloric acid.

Sodium hydroxide

Solutions were prepared directly from pellets of the solid using carbon dioxide free water, and stored in polythene bottles under nitrogen. On standardising with perchloric acid, using methyl red as indicator, no premature end points caused by the presence of carbon dioxide were found. Concentrated solutions were analysed by titrating weighed portions with perchloric acid.

Phenylacetic acid

The Eastman-Kodak product was purified by washing the molten acid with boiling water. After cooling with vigorous stirring the crystalline product was filtered off, and washed with water. The process was repeated and the acid dried in a vacuum oven at 40°C with a reduction of 25in. in pressure.

Sodium phenylacetate

A solution of sodium phenylacetate was prepared by dissolving

phenylacetic acid in concentrated sodium hydroxide solution until the pH of the solution was 6-7. The solution was analysed potentiometrically, [see Sec 2 - D - d] and found to contain 2.197Moles/1000g. This solution contained some phenylacetic acid which was determined in subsequent analysis of the buffers.

Cyanoacetic acid.

The Eastman-Kodak product was recrystallised twice from 40%/60% V/V benzene and acetone. The acid was dried first over paraffin wax, and then over calcium chloride and had a m.p. of 70.8-71.6°C. On titrating weighed portions with standard sodium hydroxide using phenolphthalein as indicator the acid was found to be 99.8% pure.

Chloroacetic acid.

Dried, weighed portions of B.D.H. AnalaR chloroacetic acid were titrated with standard sodium hydroxide using thymol blue as indicator, and proved to be 99.9% pure.

Sodium glycollate.

The B.D.H. product was purified by precipitating twice from aqueous solution by the addition of ethanol. The final product was washed with ethanol, dried at the pump, and then completely dried in a vacuum oven at 60°C with a pressure reduction of 25ins.

Methoxyacetic acid.

The Eastman Kodak acid was purified by distillation under reduced pressure using a Vigreux column. The fraction boiling at 99.5-100.5°C at 14-15 mm pressure was retained, analysed by

titration using phenolphthalein as indicator and found to be 100% pure.

Phenoxyacetic acid.

On titrating weighed, dry portions of the Eastman Kodak product it was found to have an acidity corresponding to 100.3% phenoxyacetic acid, and was used without further purification.

Mandelic acid.

Titration of dry, weighed portions of the B.D.H. racemic product with standard sodium hydroxide using phenolphthalein as indicator gave a value of 99.8$_5$% for the purity, and the acid was used without further treatment.

Copper perchlorate.

The first copper perchlorate solution used was prepared by D. L. Martin(1961) but reanalysed as follows: 5-6g. portions of solution, containing 0.2-0.3g. of copper, were weighed out, diluted to about 150ml. with water, 1 drop of 0.1N hydrochloric acid, 5 drops concentrated sulphuric acid, 1ml of concentrated nitric acid and 1g. of urea added. The copper was then determined electrolytically using platinum mesh electrodes with an independent glass stirrer. A current of 0.3A. was used for the first 5min. and then a current of 1.5A. until the electrolysis was complete, in about 45min. After the residual solution had been clear for some time it was tested for copper with diethyldithiocarbamate and the electrolysis terminated when the test was negative. The cathode was then washed with water, rinsed in alcohol and dried for 10min. in a steam oven before weighing. The acid present was determined potentiometrically. [See Sec 2 - E - d].

The second copper perchlorate solution used was prepared by suspending copper oxide in water, adding an equivalent amount of perchloric acid and heating to dissolve the oxide. Excess acid was added and the solution diluted so that the final solution was approximately 0.7M copper perchlorate containing 0.03M perchloric acid. The solution was analysed as above for copper and acid content.

The concentrations of these two solutions were 740.9mM copper perchlorate/1000g. plus 6.959mM perchloric acid/1000g., and 695.2mM copper perchloric/1000g. plus 29.539mM perchloric acid/1000g. respectively.

Copper perchlorate solutions for titrations had the composition

Copper(II) perchlorate	=	xM
Sodium perchlorate	=	(3-2x)M
Perchloric acid	=	yM

2 - B. PREPARATION OF BUFFERS.

Buffer solutions were obtained in two ways; either from the original materials or by mixing calculated amounts of buffers already prepared. Several methods of preparing the buffers from the original material were used. The series of buffers prepared for each system had a salt:acid ratio ranging from 20:1 to 1:20. The acid content of the buffers was determined volumetrically using standard sodium hydroxide, and either phenolphthalein, or thymol blue indicator.

As stated previously all solutions used in carrying out potentiometric measurements were 3.00M with respect to sodium ions.

A typical buffer with acid:salt ratio x:y would therefore have the composition,

Carboxylic acid	=	xM
Sodium carboxylate	=	yM
Sodium perchlorate	=	(3-y)M

Phenylacetate buffers.

The solubility of phenylacetic acid in 3.00M sodium perchlorate is approximately 73mM/l. at 25°C; but the solubility depends on the amount of sodium phenylacetate present (Smith 1953). Buffers were prepared by weighing out calculated amounts of the stock solutions of sodium phenylacetate, and sodium perchlorate to make the final solution 3.00M with respect to sodium ions, together with phenylacetic acid to give a final concentration of approximately 70mM (the acid content of the stock sodium salt solution being taken into account). These were made up to the correct volume at 25°C after the acid had dissolved.

Cyanoacetate buffers.

An approximately 3M solution of cyanoacetic acid in 3.00M sodium perchlorate was prepared, and analysed volumetrically. A 3.00M solution of sodium hydroxide was also prepared. Buffers were prepared by mixing the necessary volumes of these two solutions to give the required salt:acid ratio, and a final cyanoacetate concentration of 1500mM. The calculated amount of sodium perchlorate was weighed out in the empty graduated flask.

Chloroacetate, methoxyacetate, and phenyoxyacetate buffers.

An approximately 6molal solution of sodium hydroxide was analysed by weight by titration against standard perchloric acid. Buffers were prepared by partial neutralisation of weighed quantities of the acids.

Glycollate buffers.

The required quantities of sodium glycollate and 60% perchloric acid were mixed.

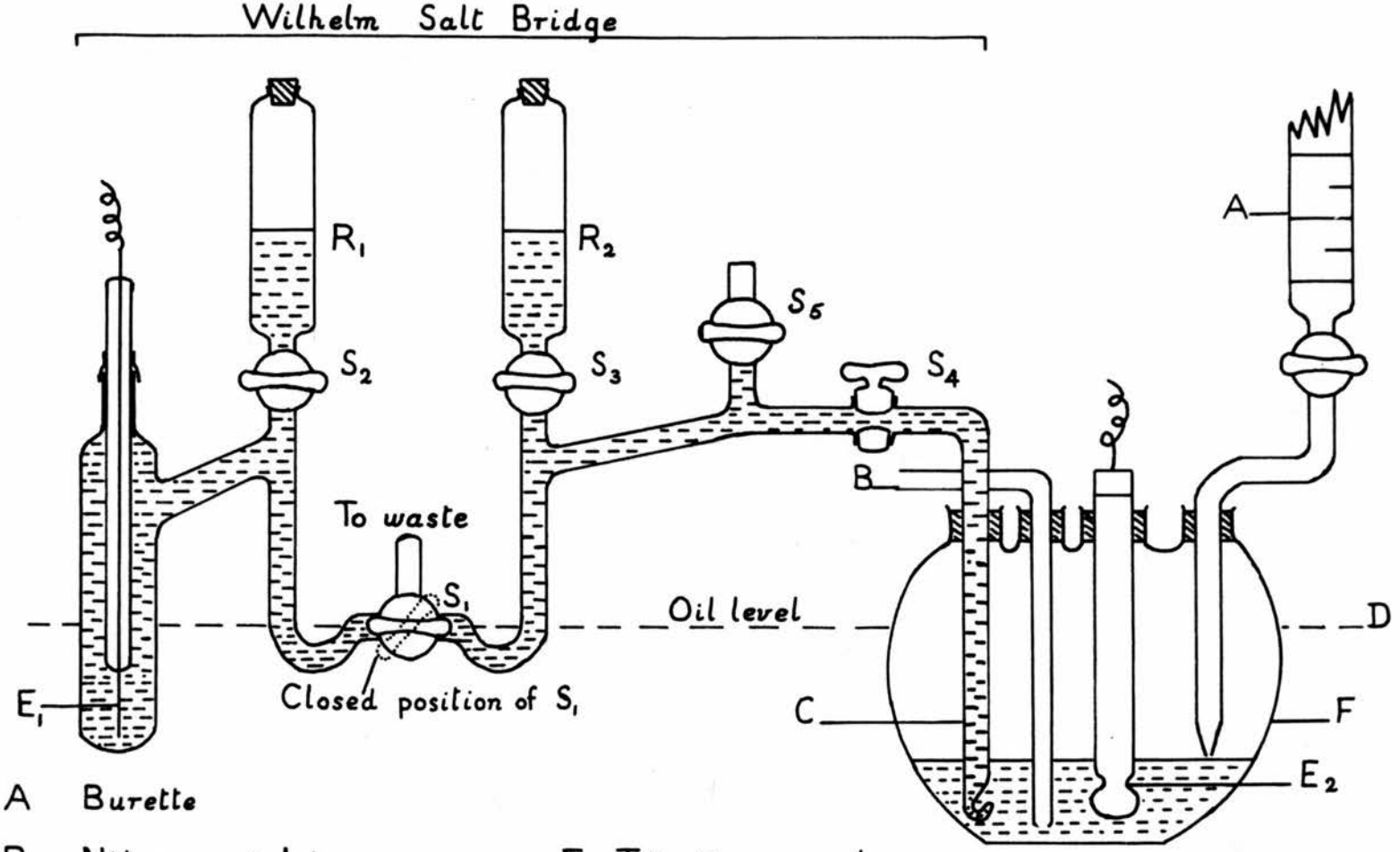
Mandelate buffers.

The solubility of mandelic acid was found to vary considerably with the amount of sodium mandelate present. A stock solution, 1400mM with respect to sodium mandelate, was therefore prepared by mixing equal proportions of mandelic acid and sodium hydroxide. A series of perchloric acid solutions, of increasing concentration, was also prepared. Buffers were then made in the titration vessel by running in equal, or proportionate, increments of the sodium mandelate solution, and the requisite perchloric acid solution to give the buffer with the salt:acid ratio required. The buffers for copper titrations were prepared in the same way as chloroacetic acid buffers.

2 - C APPARATUS.

Hard glass grade A burettes, and standard flasks were used exclusively. Solutions, other than alkaline ones, were kept in Jena, or Pyrex bottles, rubber stoppered to prevent evaporation.

FIG. 2-1 TITRATION CELL



A Burette

B Nitrogen inlet

C J-tube

E_1 Silver reference electrode

E_2 Glass electrode

F Titration vessel

R_1, R_2 Reservoirs

S_1 Three-way stopcock

S_2, S_3, S_4, S_5 Stopcocks

Alkaline solutions were kept in polythene bottles.

The potentiometric titration cell used was of the type described by Forsling, Hietanen, and Sillén(1952) and is shown in Fig. 2-1. The titration vessel, F, had a total capacity of 150ml., and had five openings to take the various fittings. The 25, or 50ml., burette, A, had an extended tip which was bent as shown to allow easier manipulation of the stopcock. The end of the nitrogen inlet, B, was partly closed by heating. The glass electrode, E_2, was a Radiometer shielded type, G202A, suitable for use over the pH range 0-9. Before use the electrode was immersed in 0.1N hydrochloric acid for 24hr., and then in distilled water for 24hr. The electrode was thereafter stored in distilled water. The treatment with acid was repeated occasionally. To ensure that the electrode was functioning correctly over the required pH range, it was tested as in Sec 2 - D - a before being used for any measurements.

The Wilhelm salt bridge consisted of two parts separated by the threeway stopcock S_1. The solution to the left of S_1, surrounding the silver reference electrode [see below] was 2.99M with respect to sodium perchlorate and 0.01M with respect to silver perchlorate. That to the right was 3.00M sodium perchlorate. These solutions were kept in the reservoirs R_1 and R_2 respectively. The salt bridge was in contact with the titration solution via the J-tube, C. The silver reference electrode was firmly held in position by a rubber sleeve.

Before each titration the liquid junction in S_1 was renewed by

suitable manipulations of the stopcocks S_1, S_2, and S_3, and the solution at the end of the J-tube renewed by temporarily closing S_1, and opening S_3 and S_4. While making measurements S_1 was open in the position to join the two halves of the salt bridge with the third opening closed, and S_4 was open thus completing the circuit. As the Wilhelm salt bridge was air-tight there was no flow of solution. The glass electrode and the reference electrode were connected to the potentiometer. Titrations were carried out with the apparatus immersed in an oil bath to the level shown by the dotted line, D.

The various pieces of equipment were firmly held in place in the titration vessel by rubber stoppers and the nitrogen was allowed to escape through a slit in the stopper holding the glass electrode. The fifth neck, which was for a second burette, was closed with a rubber stopper when not in use.

The <u>silver reference electrode</u>, E_1 was prepared by the method of Brown(1934). A platinum wire 1-2cm. long, with one end sealed through a glass tube, was coated with silver by electrolysis from a 1% solution of potassium argentocyanide, for 8hr. at 0.3mA. Free cyanide was removed from the solution before use by adding sufficient dilute silver nitrate solution to produce a faint precipitate of silver cyanide. After electrolysis the electrode was carefully washed with distilled water, and then lightly chloridized by electrolysis in a 0.1N hydrochloric acid solution for 30min. at 0.3mA, with the silver electrode as the anode. Thereafter the electrode,

which was purplish brown in colour, was kept in water until required. If the electrode was not required for some time the preparation was carried out only as far as the deposition of the silver, the last stage being carried out just prior to filling the Wilhelm salt bridge. This silver electrode was also stored in water. Such electrodes functioned satisfactorily for periods of up to one year.

The potentiometer used was a Radiometer, model PHM 3m which was calibrated against a Pye Vernier Precision potentiometer. Potentials were measured to $\pm$ 0.2mV.

Potentiometric titrations were carried out in an oil thermostat at 25.00±0.05°C. This thermostat and all solutions used in the titrations were kept in a room temperature controlled to 25.0±0.5°C.

2 - D. POTENTIOMETRIC PROCEDURE.

The complete cell used in the potentiometric measurements was

Glass	xM HA yM NaA			2.99M $NaClO_4$	silver
(-) Electrode	zM $Cu(ClO_4)_2$	3.00M $NaClO_4$		0.01M $AgClO_4$	reference (+)
	(3-y-2z)M $NaClO_4$				electrode
	wM $HClO_4$				(2-1)

In measurements on carboxylic acids Z=0.

2 - D - a) Checking of glass electrode.

Before any titrations were carried out it was necessary to check that the glass electrode followed Nernst's equation over the pH range

within which measurements would be made. This was done using the cell

(-) Glass electrode $\left| H^+Cl^- \right|$ Quinhydrone (+) (2-2)

The Nernst equation is valid for glass electrodes, and quinhydrone electrodes at pH $\leq$ 8: Using the subscripts g and q to denote the glass and quinhydrone electrode respectively, we have

$$E_g = E_{o(g)} + 59.15 \log h \qquad (2-3)$$

for the left-hand half-cell of cell (2-2) and

$$E_q = E_{o(q)} + 59.15 \log h \qquad (2-4)$$

for the right-hand half-cell. Combining Eqs. (2-3) and (2-4) gives the potential, E, of cell (2-2).

$$E = E_q - E_g = E_{o(q)} - E_{o(g)} = \text{constant} \qquad (2-5)$$

The potentiometer should therefore show a constant reading when both electrodes are immersed in solutions of pH $\leq$ 8, provided the glass electrode functions according to Nernst's equation. On carrying out an acid-base titration a constant value of 134.0mV was obtained for E above pH $\approx$ 1.5.

2 - D - b) Carboxylic acid equilibria.

Except in the phenylacetate system each titration consisted of two parts: first an acid-base titration to determine E_o and secondly the measurements on the buffer solution.

17.50ml. of approximately 10mM perchloric acid solution was titrated with sodium hydrogen carbonate solution of known concentration (approximately 100mM), the latter being added in 0.10 or 0.20ml. increments, and the potential recorded, until the pH of the buffer to

be added was reached approximately. The stream of nitrogen displaced evolved carbon dioxide. E_o was then calculated from these measurements. In the case of buffers with a low pH 0.50-0.60ml. of sodium hydrogen carbonate were added in 0.10ml. increments to give sufficient points to determine E_o.

Buffer solution of known composition was then added in small increments at first and then in larger calculated amounts such that the increase in total carboxylate concentration, A, was 50mM or 100mM. Mandelate buffers were made *in situ*. The additions of sodium mandelate and perchloric acid solutions were such that the total mandelate concentration increased by 50mM each time. Whenever possible titrations were continued up to A equal to 1000mM.

Owing to the low solubility of phenylacetic acid it was desirable to make measurements up to the total concentration of the stock buffer solutions. The titration outlined above was carried out first, buffer being added until A was somewhat more than half the stock buffer concentration. Next a known volume of pure buffer was diluted with 3.00M sodium perchlorate, the potential being recorded at concentration intervals as before. By making measurements at a series of similar concentrations in both parts of these titrations, it was possible to ascertain whether any change in E_o had occurred while changing the glass electrode over. The readings common to the two parts would show a fixed difference if any change had occurred, and those from the dilution measurements could be related to the same value of E_o as the first readings.

2 - D - c) Copper carboxylate equilibria.

Except in the cyanoacetate and chloroacetate systems the method was similar to the previous one but with copper present either at a variable or a fixed concentration. The methods used are illustrated by the following generalised examples.

8.50ml. of perchloric acid of known concentration (10-20mM) and 8.50ml. of copper perchlorate solution, twice the concentration being used in the titration, containing a known amount of perchloric acid were mixed and E_o found by titrating with standard sodium hydrogen carbonate. The copper concn was held constant by adding equal volumes of the copper perchlorate solution. This preliminary titration was stopped when the pH of the solution was 1-1.5pH units below that of the buffer to be added, Buffer solution and copper perchlorate solution were then added in suitable equal volumes such that E changed by a few mV each time. This was continued either until a precipitate appeared or large increments of buffer produced only small changes in pH.

When the copper concentration was allowed to vary the initial solution was prepared by diluting a 200mM copper perchlorate solution with 3.00M sodium perchlorate and 50mM perchloric acid. The procedure was then as before, omitting the additions of copper perchlorate. This method was particularly useful when buffers with a small A had to be used, or where high free ligand concentrations were necessary.

Owing to the somewhat low pH of cyanoacetate and chloracetate buffers it was necessary to start the second part of the copper

carboxylate titrations at pH ~ 2. E_o was therefore determined by adding standard perchloric acid (~50mM) to a mixture of 200mM copper perchlorate and 3.00M sodium perchlorate, the copper concentration being allowed to vary. Buffer solution was then added in suitable increments.

The usual method of calculating E_o could not be applied in these cases since the first part was not the usual acid-base titration. [See Sec 3 - A for both methods].

2 - D - d) Miscellaneous titrations.

(i) Determination of the concentration of sodium phenylacetate:

As the concentration of the solution was known within ± 1% a solution approximately 0.5M with respect to sodium phenylacetate and 3M with respect to sodium ions was prepared.

17.50ml. of 16mM perchloric acid was titrated with 99.64mM sodium hydrogen carbonate solution to determine E_o. 4.00ml. of the sodium phenylacetate solution was then added and titrated with 100.1mM perchloric acid until all the salt had been converted to acid.

From the results of this analysis it was possible to prepare a solution more precisely 0.5M with respect to sodium phenylacetate and 3.00M with respect to sodium ions. A second analysis was then carried out and found to be in good agreement with the first.

The method of calculation is given in Sec 3 - C.

(ii) Determination of the acidity of copper perchlorate solutions.

A known volume of the stock copper perchlorate solution was titrated with standard sodium bicarbonate solution using the normal

titration assembly. The end point was found by Gran's method (Sec 3 - 1) and checked by the constancy of E_o.

(iii) Mononuclear formation curve for phenoxyacetic acid.

17.50ml. of 10mM perchloric acid was titrated with 0.50ml. of 99.09mM sodium hydroxide solution, added in 0.10ml. increments to give six points to determine E_o. 18.00ml. of 40.03mM phenoxyacetic acid solution was then added and the addition of sodium hydroxide continued in increments such that there was a change of 6-10 mV each time to the end point.

CHAPTER 3.

METHODS OF CALCULATION.

3 - A. DETERMINATION OF E_o.

For cells of the type (2-1) the relationship between the measured potential, E(in mV), and the concentration of free hydrogen ions h at 25°C is given by

$$E = E_o + E_j - 59.15\log h \qquad (3\text{-}1)$$

The term E_o is the difference between the standard potentials of the two electrodes plus the asymmetry potential of the glass electrode, minus $59.15\log \gamma_H$. E_j is the liquid junction potential but has been shown (Biedermann and Sillén 1953; Rossotti and Rossotti 1956) to be less than the experimental uncertainty in E, $\pm$ 0.2mV, for $h \leq 10mM$ and can therefore be neglected, giving

$$E = E_o - 59.15\log h \qquad (3\text{-}2)$$

E_o is obtained from the results of the preliminary acid-base titration, the end point being found by Gran's(1952) method. $V_A$ml. of acid, of concentration C_H, is placed in the titration pot and $V_B$ml. of standard alkali of concentration C_B, added. At any point during the titration

$$h = \frac{V_A C_H - V_B C_B}{V_A + V_B} \qquad (3\text{-}3)$$

At the equivalence point when V_e ml. of alkali have been added

$$V_A C_H = V_e C_B \qquad (3\text{-}4)$$

and combining Eqs. (3-3) and (3-4)

$$h = \frac{C_B(V_e - V_B)}{V_A + V_B} \qquad (3\text{-}5)$$

Now, as E_o is unknown, an arbitrary constant E_o' is substituted in Eq. (3-2) which is rearranged to give

$$h = 10^{(E_o' - E)/59.15} \qquad (3\text{-}6)$$

Combining Eqs. (3-5) and (3-6) gives

$$(V_A + V_B)10^{(E_o'-E)/59.15} = C_B(V_e - V_B) \qquad (3\text{-}7)$$

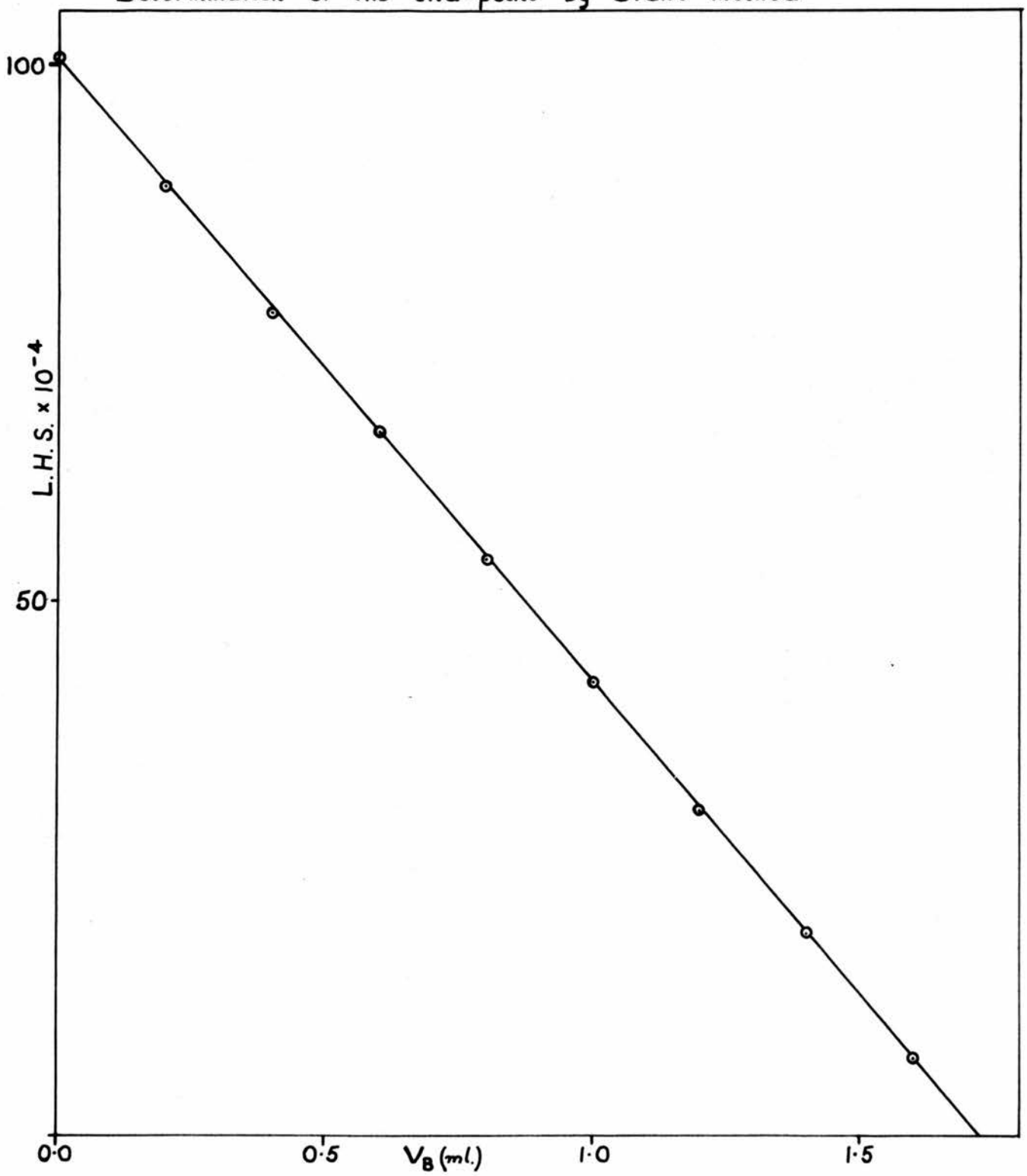
A plot of the left hand side of Eq. (3-7) against V_B gives a straight line with intercept V_e on the V_B axis.

Values of h can then be calculated from Eq. (3-5) for each point in the titration and the corresponding values of E_o obtained from Eq. (3-2). The average value of E_o is used in ensuing calculations. Data for a determination of E_o are shown in Table 3-1 and the corresponding Gran plot in Fig. 3-1.

In those instances where E_o had to be determined by adding standard acid to a slightly acidic solution of copper(II) perchlorate there was no primary graphical step in the calculations. If the initial volume of copper(II) perchlorate in the titration vessel,

FIG. 3-1 ACID-BASE POTENTIOMETRIC TITRATION

Determination of the end-point by Gran's method



V_{Cu}ml., has an acid concentration h_{Cu}, and $V_A$ml. of perchloric acid, concentration C_H added, then

$$h = \frac{h_{Cu} V_{Cu} + V_A C_H}{V_{Cu} + V_A} \qquad (3\text{-}8)$$

From the increments of standard acid added a series of values of h and the corresponding values of E_o were obtained.

Table 3-1.

$V_B$ml.	$V_A + V_B$ml.	EmV	L.H.S.	log h	E_omV
0.00	17.50	218.5	100.5	0.9950	277.4
0.20	17.70	222.0	88.69	0.9365	277.4
0.40	17.90	226.0	76.78	0.8706	277.5
0.60	18.10	230.3	65.66	0.7947	277.3
0.80	18.30	235.7	53.80	0.7050	277.4
1.00	18.50	242.1	42.39	0.5944	277.3
1.20	18.70	250.9	30.42	0.4497	277.5
1.40	18.90	263.5	18.82	0.2367	277.5
1.60	19.10	288.2	7.27	-0.1831	277.4

Average E_o = 277.4

L.H.S. = left hand side of Eq. (3-7)x10^{-4}, where 500 has been used as the arbitrary value of E_o'.

C_B = 100.3mM

V_e = 1.725mM

C_H = 9.88_7mM

Here and elsewhere h has been expressed in millimoles/l^{-1} for convenience.

3 - B. METHODS OF COMPUTATION - INTRODUCTION.

Just as there are many experimental procedures available, and being developed, for studying complex formation in solution, so there is an increasing volume of literature on methods of computing stability constants from the data obtained. The majority of these procedures and methods have been fully described, and their merits assessed by Rossotti and Rossotti(1961a).

Data, as accurate as possible, and covering a wide range of the concentration variables are a desirable prerequisite to computing stability constants. Further, it should always be ascertained that the results are reproducible, that they refer to systems at equilibrium, and that no untoward precipitation has occurred. The final interpretation of the data should be in terms of the minimum number of parameters which best explain all the experimental measurements. Graphical methods of determining the values of the constants have the advantage that much, or all, of the experimental data can be considered simultaneously, and realistic limits of error ascribed to the stability constants obtained. A number of such methods have been used in the present work and they are described below with particular reference to the systems to which they have been applied.

It has been assumed that the activity coefficients of all the species can be held effectively constant, so that the law of mass action can be applied to the concentrations of the reacting species to obtain stoichiometric stability constants.

3 - C. CURVE FITTING TECHNIQUES FOR ACID SYSTEMS.

The first step in interpreting the experimental results is to prepare formation curves from the data on hand. In the acid systems these are $\bar{n}$(log h) curves. Log h is readily obtained from Eq.(3-2) as E is measured, E_o is found from the preliminary titration, and $\bar{n}$ is subsequently calculated from the expression

$$\bar{n} = \frac{H - h + K_w h^{-1}}{A} \qquad (3\text{-}9)$$

where H, the total hydrogen ion concentration, consists of the concentration of carboxylic acid added, C_{HA}, plus the contribution from C_H' the concentration of perchloric acid in the titration vessel at the end of the E_o determination; and K_w is the ionic product of water. The term $K_w h^{-1}$ is very small for $h > 10^{-7}$M, and may be neglected. This gives, where V_T is the total volume in the titration vessel and V_i the volume at the end of the E_o determination,

$$\bar{n} = \frac{C_{HA} + C_H' \frac{V_i}{V_T} - h}{A} \qquad (3\text{-}10)$$

The $\bar{n}$ concept was also used in calculating the concentration of sodium phenylacetate in the stock solution. At any point during the titration of sodium phenylacetate with perchloric acid, we have

$$\bar{n} = \frac{(C_{HA} + C_H')\frac{V_i}{V_T} + C_H \frac{V_A}{V_T} - h}{(C_{HA} + C_A)\frac{V_i}{V_T}} \qquad (3\text{-}11)$$

All the symbols have been defined previously except C_A, the concentration of sodium carboxylate. At the end point $\bar{n} = 1.00$, whence

$$C_A = C_H \frac{V_A}{V_i} - h\frac{V_T}{V_i} + C'_H \qquad (3\text{-}12)$$

When all the sodium salt has been neutralised the expression on the right hand side of Eq.(3-12) remains constant as more acid is added. This constant value is the initial concentration of sodium carboxylate.

The formation of complexes in systems will now be considered in the following sections.

3 - C - a. Formation of one complex.

When the only species present, other than the free ligand and hydrogen ions, is the monomeric acid HA, then

$$H = h + HA = h + \beta_{11} ha \qquad (3\text{-}13)$$

$$A = a + HA = a + \beta_{11} ha \qquad (3\text{-}14)$$

Therefore, from (3-9)

$$\bar{n} = \frac{\beta_{11} h}{1 + \beta_{11} h} = \frac{h^*}{1 + h^*} \qquad (3\text{-}15)$$

where

$$\log h^* = \log \beta_{11} + \log h \qquad (3\text{-}16)$$

$\bar{n}$ is thus a function of the normalised variable h^* only (c.f. Sillén 1956a). The curve $\frac{h^*}{1 + h^*}(\log h^*)$ is calculated and the experimental

plot $\bar{n}$(log h) compared with it to obtain the position of best fit. The value of log h at log h* = 0 then gives the value of -log β_{11}; i.e. when n = $\frac{1}{2}$, -log h = log β_{11}. This technique was employed to find β_{11} for all the acids investigated. The limits of error in log β_{11} are obtained by finding the maximum horizontal distance through which the experimental curve may be moved while keeping the theoretical curve within the experimental uncertainty.

3 - C - b. Formation of more than one complex.

At A $\gtrsim$ 50mM it was apparent that species other than HA were present, and that these species were polynuclear as the value of $\bar{n}$, at a given value of log h, was a function of A. The data were accordingly analysed using families of normalised curves of the type log A*(log h*)$_{\bar{n}}$ (Sillén 1956b). Similar methods have been used successfully in the study of inorganic polyanions, and the hydrolysis of metal ions. (e.g. Ingri et al. 1957; Rossotti and Rossotti 1956; Biedermann et al. 1956; Ingri and Brito 1959).

In the derivation of the following families of curves applicable to the systems studied charges have been omitted for clarity.

(i) Normalised curves for the system A, HA, H_2A_2.

The mass balance equations for a system containing A, HA and H_2A_2 are

$$A = a + [HA] + 2[H_2A_2]$$

$$= a + \beta_{11}ha + 2\beta_{22}h^2a^2 \qquad (3\text{-}17)$$

$$H = h + [HA] + 2[H_2A_2]$$

$$= h + \beta_{11}ha + 2\beta_{22}h^2a^2 \qquad (3\text{-}18)$$

Combination of Eqs.(3-9) and (3-18) gives

$$A\bar{n} = \beta_{11}ha + 2\beta_{22}h^2a^2 \qquad (3\text{-}19)$$

By subtracting Eq.(3-19) from Eq.(3-17) we obtain

$$A(1 - \bar{n}) = a \qquad (3\text{-}20)$$

Substitution of Eq.(3-20) into Eq.(3-19) gives

$$\frac{\bar{n}}{(1 - \bar{n})h} = \beta_{11} + 2\beta_{22}A(1-\bar{n})h \qquad (3\text{-}21)$$

a linear function from which values of β_{11} and β_{22} can be calculated.

It is more convenient, however, if a general family of curves with which to compare each system investigated is available. Such is the case when normalisation is carried out.

Setting $h^* = \beta_{11}h$ (3-22)

and $A^*/A = \beta_{22}/\beta_{11}^2$ (3-23)

we obtain on substituting into Eq.(3-21) and simplifying

$$A^* = \frac{\bar{n} - h^*(1 - \bar{n})}{2(h^*)^2(1 - \bar{n})^2} \qquad (3\text{-}24)$$

The experimental data $\log A(\log h)_{\bar{n}}$ [See Sec 4] are superimposed on the family of $\log A^*(\log h^*)_{\bar{n}}$ curves and the position of best fit obtained. The values of the stability constants are found using Eqs.(3-22) and (3-23) in the forms

$$\log h^* - \log h = \log \beta_{11} \qquad (3\text{-}25)$$

$$\log A^* - \log A = \log \beta_{22} - 2\log \beta_{11} \qquad (3\text{-}26)$$

respectively.

In this and similar cases to be described the maximum limits of error in the values of the functions obtained are given by the permissible vertical and horizontal displacement of the origin of the normalised curves whilst maintaining an acceptable fit.

(ii) Normalised curves for the system A, HA, HA_2, H_2A_2.

Previous work on carboxylic acids (Martin 1961) indicated that the species present could be A, HA, HA_2, H_2A_2. In such a system we have

$$A = a + [HA] + 2[HA_2] + 2[H_2A_2]$$

$$= a + \beta_{11}ha + 2\beta_{12}ha^2 + 2\beta_{22}h^2a^2 \qquad (3\text{-}27)$$

$$H = h + [HA] + [HA_2] + 2[H_2A_2]$$

$$= h + \beta_{11}ha + \beta_{12}ha^2 + 2\beta_{22}h^2a^2 \qquad (3\text{-}28)$$

Combination of Eqs.(3-9) and (3-28) gives

$$A\bar{n} = \beta_{11}ha + \beta_{12}ha^2 + 2\beta_{22}h^2a^2 \qquad (3\text{-}29)$$

Equations (3-27) and (3-29) are normalised by setting

$$h^* = \beta_{11}h \qquad (3\text{-}22)$$

$$A^*/A = v/a = \beta_{12}/\beta_{11} \qquad (3\text{-}30)$$

$$R = \beta_{22}/\beta_{11}\beta_{12} \qquad (3\text{-}31)$$

Thus we obtain from Eq.(3-27)

$$A^* = (1 + h^*)v + 2h^*(1 + Rh^*)v^2 \qquad (3\text{-}32)$$

and from Eq.(3-29)

$$A^*\bar{n} = h^*v + h^*(1 + 2Rh^*)v^2 \qquad (3\text{-}33)$$

Subtracting Eqs.(3-33) from Eq.(3-32)x$\bar{n}$ and solving for v gives

$$v = \frac{h^* - (1 + h^*)\bar{n}}{h^*[2\bar{n}(1 + Rh^*) - (1 + 2Rh^*)]} \qquad (3\text{-}34)$$

When Eq.(3-34) is substituted in Eq.(3-32)

$$A^* = \frac{[\bar{n} + h^*(\bar{n}-1)][1 + (2R - 1)h^*]}{h^*[2R(1 - \bar{n})h^* + 1 - 2\bar{n}]^2} \qquad (3\text{-}35)$$

In cases where an isohydric point, (a point where all the formation curves intersect), occurs the degrees of formation of monomer and dimers are equal, and it is possible to evaluate R from the position of this point. If we take $\bar{n}_c$ to be the value of n at the isohydric point, and $\bar{n}_1$ and $\bar{n}_2$ to be the degrees of formation of monomer and dimers respectively, we get, using the above normalisations

$$\bar{n}_c = \bar{n}_1 = \frac{\beta_{11}h}{1 + \beta_{11}h} = \frac{h^*}{1 + h^*} \qquad (3\text{-}36)$$

$$\bar{n}_c = \bar{n}_2 = \frac{\beta_{12} + 2\beta_{22}h}{2\beta_{12} + 2\beta_{22}h} = \frac{1 + 2Rh^*}{2 + 2Rh^*} \qquad (3\text{-}37)$$

On solving Eq.(3-37) for R and eliminating h^* using (3-36)

$$R = \frac{2\bar{n}_c - 1}{2\bar{n}_c} \qquad (3\text{-}38)$$

Therefore when R can be calculated from Eq.(3-38), the experimental data in the form log $A(\log h)_{\bar{n}}$ are placed in the position of best fit on the family of log $A^*(\log h^*)_{\bar{n},R}$ curves and the stability constants evaluated from this fit. Log β_{11} is found from Eq.(3-25), and log β_{12} and β_{22} from Eqs.(3-30) and (3-31) in the forms

$$\log A^* - \log A = \log \beta_{12} - \log \beta_{11} \qquad (3\text{-}39)$$

$$\log R + \log \beta_{11} + \log \beta_{12} = \log \beta_{22} \qquad (3\text{-}40)$$

In cases where there is no isohydric point within the range of the experimental data R must be found by successive approximations. This entails preparing several sets of log $A^*(\log h^*)_{\bar{n},R}$ curves using different values of R with which to compare the results.

In addition to the overall stability constants obtained above the stepwise constants for reactions (1-18), (1-19) and (1-15) can now be evaluated as follows

$$\log K_{12} = \log \beta_{12} - \log \beta_{11} = \log A^* - \log A \qquad (3\text{-}39a)$$

$$\log K_{22} = \log \beta_{22} - \log \beta_{12} = \log R + \log \beta_{11} \qquad (3\text{-}41)$$

$$\log K_D = \log \beta_{22} - 2 \log \beta_{11}$$

$$= \log R + \log \beta_{12} - \log \beta_{11} = \log R + \log K_{12} \qquad (3\text{-}42)$$

The errors in these latter functions are calculated from the errors in the functions from which they are obtained.

(iii) Normalised curves for the system A, HA, HA_2, H_2A_3.

In the case of mandelic acid the curvature of the log $A(\log h)_{\bar{n}}$ plots was greater than found in systems where association only went as far as dimerisation, and was consistent with the formation of trimeric species. At $\bar{n} \leq 0.3$ it is very probable that the species present are A, HA, HA_2, H_2A_3. Hence we have, by extending Eqs.(3-27) and (3-29)

$$A = a + \beta_{11}ha + 2\beta_{12}ha^2 + 3\beta_{23}h^2a^3 \qquad (3\text{-}43)$$

$$A\bar{n} = \beta_{11}ha + \beta_{12}ha^2 + 2\beta_{23}h^2a^3 \qquad (3\text{-}44)$$

Equations (3-43) and (3-44) are normalised using Eqs.(3-22) and (3-30), and

$$R = \beta_{23}/\beta_{12}^2 \qquad (3\text{-}45)$$

whence

$$A^* = (1 + h^*)v + h^*v^2(2 + 3Rh^*v) \qquad (3\text{-}47)$$

$$A^*\bar{n} = h^*v + h^*v^2(1 + 2Rh^*v) \qquad (3\text{-}48)$$

Multiplying (3-47) by 2 and subtracting (3-48) x 3 gives

$$A^*(2 - 3\bar{n}) = (2 - h^*)v + h^*v^2 \qquad (3\text{-}49)$$

On solving this quadratic equation for v we get

$$v = \left[h^* - 2 + \sqrt{(2 - h^*)^2 + 4h^*A^*(2 - 3\bar{n})}\right] \Big/ 2h^* \qquad (3\text{-}50)$$

Subtracting Eq.(3-47) x $\bar{n}$ from Eq.(3-48)

$$h^* - \bar{n}(1 + h^*) + R(h^*)^2v^2(2 - 3\bar{n}) + hv(1 - 2\bar{n}) = 0 \qquad (3\text{-}51)$$

whence

$$v = \frac{(2\bar{n}-1) + \sqrt{(1-2\bar{n})^2 - 4R(2-3\bar{n})[h^* - (1+h^*)\bar{n}]}}{2h^*R(2-3\bar{n})} \qquad (3\text{-}52)$$

By equating Eqs.(3-50) and (3-52) an expression for A* is obtained

$$2Rh^*(2-3\bar{n})^2A^* = \frac{(2\bar{n}-1)^2}{R(2-3\bar{n})} + 6\bar{n} - (2+h^*) \qquad (3\text{-}53)$$

$$+\sqrt{(1-2\bar{n})^2 - 4R(2-3\bar{n})[h^*(1-\bar{n}) - \bar{n}]}\left[\frac{2\bar{n}-1}{R(2-3\bar{n})} + 2 - h^*\right]$$

Families of log A*(log h*)$_{\bar{n},R}$ curves for different values of R are prepared and the best fit for the experimental data log A(log h)$_{\bar{n}}$ found. Stability constants and errors are computed in an analogous manner to those in the previous normalisation.

3 - D. AVERAGE COMPOSITION OF POLYNUCLEAR SPECIES BY INTEGRATION.

A fairly reliable indication of the extent of polymerisation may be obtained by eliminating the mononuclear terms from expressions for $\bar{p}$ and $\bar{q}$, which are the average number of ligands, and central group per complex, respectively, and are given by

$$\bar{p} = \frac{\sum_{1}^{P}\sum_{1}^{Q} p[H_pA_q]}{\sum_{0}^{P}\sum_{1}^{Q}[H_pA_q] - a} \qquad (3\text{-}54)$$

and

$$\bar{q} = \frac{\sum_{0}^{P}\sum_{1}^{Q} q[H_pA_q] - a}{\sum_{0}^{P}\sum_{1}^{Q}[H_pA_q] - a} \qquad (3\text{-}55)$$

The average composition of the polynuclear species can then be obtained from the experimental $\bar{n}(\log h)_A$ curves without making any special assumptions about the complexes formed.

It is convenient to break up a number of the primary and secondary concentration variables into separate terms for each value of q. Thus

$$A = A_1 + A_{poly} \tag{3-56}$$

$$A\bar{n} = A_1\bar{n}_1 + A_{poly}\bar{n}_{poly} \tag{3-57}$$

$$A\bar{r} = A_1 + A_{poly}\bar{r}_{poly} \tag{3-58}$$

where the subscript 'poly' denotes terms which refer to polynuclear species only, and 1 refers to mononuclear terms i.e. A and HA; $\bar{r}$ is the reciprocal of the average degree of condensation of all species which contain A.

Using Eqs.(3-56), (3-57) and (3-58) we obtain

$$\bar{p}_{poly} = \frac{\bar{n}_{poly}}{\bar{r}_{poly}} = \frac{A\bar{n} - A_1\bar{n}_1}{A\bar{r} - A_1} \tag{3-59}$$

$$\bar{q}_{poly} = \frac{1}{\bar{r}_{poly}} = \frac{A - A_1}{A\bar{r} - A_1} \tag{3-60}$$

The terms A_1 and $\bar{r}$ are obtained by means of formula derived by Sillén (unpublished), quoted by Ingri *et al.*(1957) and given in full by Rossotti and Rossotti(1961a, pp 351, 349). These formulae are

$$\log A_1 = \log A - \left\{\int_{\log h_1}^{\log h_2} [\bar{n} - \bar{n}_1 + \left(\frac{\partial \bar{n}}{\partial \ln A}\right)_h] d\log h\right\}_A \tag{3-61}$$

$$\bar{r} = 1 - \left[\int_{\log h_1}^{\log h_2} \left(\frac{\partial \bar{n}}{\partial \log A} \right)_h d\log h \right]_A \qquad (3\text{-}62)$$

A_1 and $\bar{r}$ are found by plotting $\left[\bar{n} - \bar{n}_1 + \left(\frac{\partial \bar{n}}{\partial \ln A} \right)_h \right]_A$ and $\left[\left(\frac{\partial \bar{n}}{\partial \log A} \right)_h \right]_A$ respectively against log h and evaluating the integrals graphically.

3 - E. ARITHMETICAL TREATMENT AND CALCULATION OF FORMATION CURVES.

3 - E - a) Computation of constants.

This section deals with a system containing all species up to, and including, trimers within the concentration limits of the measurements.

In systems containing A, HA, HA_2, H_2A_3 it is often possible to fit the experimental data $\log A(\log h)_{\bar{n}}$ to families of curves $\log A^*(\log h^*)_{\bar{n},R}$ with somewhat wide limits of R. In addition the stability constants for the species H_2A_2 and H_3A_3 which are present in increasing amounts when $\bar{n} \geq 0.3$ have subsequently to be determined. Two methods have been developed for computing the constants in such a case.

The first method makes use of the fact that the $\log A^*(\log H^*)_{\bar{n},R}$ curves for the system A, HA, HA_2, H_2A_2 vary only slightly at low values of A* over a wide range of values of R.

It has been found that the experimental data will fit almost any set of such curves for $A \leq 200$mM. Also $A^* = \beta_{12}A/\beta_{11}$ in both the normalisation for the above system and the normalisation for the system A, HA, HA_2, H_2A_3. Therefore by fitting the experimental data

simultaneously to curves from both normalisations with the axes coincident it is possible to get the value of β_{12}. Because of the uncertainty in R for either normalisation β_{22} and β_{23} cannot be found with any degree of certainty. The treatment of the data is hereafter purely arithmetical.

At $\bar{n} \leq 0.3$ the species present are A, HA, HA_2, H_2A_3, and

$$A = a + \beta_{11}ha + 2\beta_{12}ha^2 + 3\beta_{23}h^2a^3 \qquad (3\text{-}63)$$

$$A\bar{n} = \beta_{11}ha + \beta_{12}ha^2 + 2\beta_{23}h^2a^3 \qquad (3\text{-}64)$$

This assumption was later justified by calculating the relative amounts of the species. The contribution of the neutral species was found to be negligible.

Therefore, on subtracting Eq.(3-64) from Eq.(3-63)

$$A(1-\bar{n}) = a + \beta_{12}ha^2 + \beta_{23}h^2a^3 \qquad (3\text{-}65)$$

Using the value of β_{12} found above and a number of experimental values of $A,\bar{n}$ and h these equations are solved for β_{23}.

At $\bar{n} > 0.3$ all species have to be considered, and Eqs.(3-63) and (3-64) are extended to

$$A = a + \beta_{11}ha + 2\beta_{12}ha^2 + 2\beta_{22}h^2a^2 + 3\beta_{23}h^2a^3 + 3\beta_{33}h^3a^3 \qquad (3\text{-}66)$$

$$A\bar{n} = \beta_{11}ha + \beta_{12}ha^2 + 2\beta_{22}h^2a^2 + 2\beta_{23}h^2a^3 + 3\beta_{33}h^3a^3 \qquad (3\text{-}67)$$

Subtraction again gives Eq.(3-65) and rearrangement of Eq.(3-66) gives

$$\beta_{22} + \frac{3}{2}\beta_{33}ha = [A - a - \beta_{11}ha - 2\beta_{12}ha^2 - 3\beta_{23}h^2a^3]/2h^2a^2 \qquad (3\text{-}68)$$

As β_{23} has been obtained from the experimental data for $\bar{n} \leq 0.3$, a is now the only unknown in Eq.(3-65). Using data for $\bar{n} \geq 0.6$ values of a and the right hand side of Eq.(3-68) are computed. A plot of the latter against ha gives β_{22} as intercept and the slope is $3\beta_{33}/2$.

The second method makes no preliminary use of curve fitting other than to find β_{11}[cf. Eq.(3-16)]. The degree of polymerisation is also checked by finding $\bar{p}_{poly}$ and $\bar{q}_{poly}$. Having thereby confirmed that the highest complexes present are H_2A_3 and H_3A_3, Eqs.(3-66), (3-67), and (3-65) are applicable. Rearrangement of Eq.(3-65) gives

$$\beta_{12} + \beta_{23}ha = [A(1-\bar{n}) - a]/ha \qquad (3\text{-}69)$$

Values of a at experimental points are obtained by a graphical integration procedure using the formula

$$\log \frac{A}{a} = \left\{ \int_{\log h_1}^{\log h_2} \left[\bar{n} + \left(\frac{\partial \bar{n}}{\partial \ln A} \right)_h \right] d\log h \right\}_A \qquad (3\text{-}70)$$

given by Rossotti and Rossotti(1961a, p 347). A plot of the right hand side of Eq.(3-69) against ha gives β_{12} as intercept and β_{23}

as slope. β_{22} and β_{33} are then found as before using Eq.(3-68).

3 - E - b) Calculation of $\log A(\log h)_{\bar{n}}$ curves for a given set of constants.

After a set of constants for the system A, HA, HA_2, H_2A_2, H_2A_3, H_3A_3 has been obtained as described in the preceding section, a check is made by comparing $\log A(\log h)_{\bar{n}}$ curves, calculated by substituting the values of the stability constants into Eqs.(3-66) and (3-67), with the experimental data.

The variables in Eqs.(3-66) and (3-67) are A, a, h, and $\bar{n}$. Of these A and h can be varied independently but, having fixed those, the corresponding values of a and $\bar{n}$ are fixed. Since the equation for $\bar{n}$ involves all the variables it is not possible to calculate $\log A(\log h)_{\bar{n}}$ curves directly; these must be obtained by first calculating $\bar{n}(\log h)_A$ curves from which the former are prepared in the same way as experimental $\log A(\log h)_{\bar{n}}$ curves [See Sec 4].

The value of a corresponding to fixed values of A and h is found more quickly from Eq.(3-66) by successive approximation than by solving the cubic equation. Using the values of A, h and a, $\bar{n}$ is calculated from Eq.(3-67). This process is repeated using the same value of A but different values of h until a complete $\bar{n}(\log h)_A$ curve is obtained. A series of these curves is prepared, and then the $\log A(\log h)_{\bar{n}}$ set, with which the experimental data are compared.

3 - F. RELATIVE AMOUNTS OF SPECIES PRESENT IN ACID SYSTEMS.

The proportion, α_{pq}, of carboxylate in the form of the various species present in a system can be readily calculated as a function of the free hydrogen ion concentration.

$$\alpha_{pq} = q[H_pA_q]/A = q\beta_{pq}h^pa^q/A \qquad (3\text{-}71)$$

Thus, if α_{01} is proportion present as a, then;

$$\alpha_{01} = a/A, \text{ and } \alpha_{11} = \beta_{11}ha/A, \ \alpha_{12} = 2\beta_{12}ha^2/A, \ldots, \ \alpha_{PQ} = Q\beta_{PQ}h^Pa^Q/A \qquad (3\text{-}72)$$

When a system contains only monomers and dimers a can be found from the quadratic equation obtained by subtracting Eq.(3-29) from Eq.(3-27), i.e.

$$A(1-\bar{n}) = a + \beta_{12}ha^2 \qquad (3\text{-}73)$$

For systems containing trimers also, the analogous expression is the cubic equation, Eq.(3-65).

In practice, it was less tedious to work with Eqs.(3-27) and (3-66) respectively and find a by successive approximation. For example A was fixed at 700mM and h was varied within the limits of the experimental measurements. For any given value of h, a was adjusted until the summation of the right hand side of Eq.(3-27) or Eq.(3-66) became equal to 700 $\pm$ 1mM. The proportions were then immediately obtainable from the terms in the summation. The correct value of a was usually found at the third or fourth refinement.

3 - G. CURVE FITTING IN COPPER SYSTEMS.

3 - G - a) Form of the experimental data - $\bar{n}$(log a) curves.

In this and the following section [i.e. Secs 2 - G and 2 - F] the definition of $\bar{n}$ is slightly different from that previously used. It still refers to the number of ligands per central group but now implies the average number of carboxylate groups per central copper(II) ion. In instances where $\bar{n}$ is required both in this and the previous sense (the average number of hydrogen ions per central carboxylate group) the latter will be denoted by $\bar{n}_H$.

As a carboxylic acid-sodium carboxylate buffer is added to the copper perchlorate solution, proton-carboxylate and copper-carboxylate complex formation occur simultaneously. It is assumed that the system involving the carboxylic ions and protons is the same as that encountered while studying the carboxylic acids; and that mixed species, e.g. $B(HA_2)$ are not formed.

This assumption is subsequently confirmed as the experimental functions $\bar{n}$(log a) are independent of the buffer ratio. When calculating values of $\bar{n}$ and log a from the experimental data, such species H_pA_q, as are present at the concentration of A to which the data refer, have, therefore, to be taken into account. Thus [cf. Eq.(3-9)]

$$\bar{n}_H = \frac{H - h}{A - \bar{n}B} \qquad (3\text{-}74)$$

whence

$$A - \bar{n}B = (H-h)/\bar{n}_H \qquad (3\text{-}75)$$

or

$$\bar{n} = (A - \frac{H-h}{\bar{n}_H})/B$$

At low concentrations of carboxylate where $(A-\bar{n}B)$ is less than the concentration at which polynuclear complexes first appear in the corresponding acid system $\bar{n}_H$ is obtained from the mononuclear $\bar{n}_H(\log h)$ curve for the acid. The value of log h is derived from the measured potential, and $\bar{n}$ is then obtained from Eq.(3-76). At higher concentrations, where $\bar{n}_H$ varies with A at a fixed pH, successive approximation is used. For example, A, H, and h are known, and a reasonable estimate of $\bar{n}$ is made by reference to the previous point. The value of $\bar{n}_H$ corresponding to the estimated value of $(A-\bar{n}B)$ is then obtained from the $\bar{n}_H(\log h)_A$ curves for the acid, often by interpolation from such experimental data as have been plotted in the form $\bar{n}_H(\log h)_A$. By using Eq.(3-75) a more precise value of $(A-\bar{n}B)$ is found and the value of $\bar{n}_H$ refined. The process is continued until $\bar{n}$ and $\bar{n}_H$ are consistent. With practice the correct value is usually found in the second cycle of calculation.

The next step is the calculation of the values of a corresponding to experimental points. At low carboxylate concentrations where only monomeric acid species are present

$$A-\bar{n}B = a + \beta_{11}ha \qquad (3-77)$$

$$H = h + \beta_{11}ha \qquad (3-78)$$

Subtraction of Eq.(3-78) from Eq.(3-77) and rearrangement gives

$$a = A-\bar{n}B - (H-h) \qquad (3-79)$$

Whence, using Eq.(3-74)

$$a = \frac{H-h}{\bar{n}_H} - (H-h) \qquad (3\text{-}80)$$

In those systems which contain the species HA_2 and H_2A_2 at higher concentrations, we have

$$A-nB = a + \beta_{11}ha + 2\beta_{12}ha^2 + 2\beta_{22}h^2a^2 \qquad (3\text{-}81)$$

and

$$H = h + \beta_{11}ha + \beta_{12}ha^2 + 2\beta_{22}h^2a^2 \qquad (3\text{-}82)$$

On subtracting Eq.(3-82) from Eq.(3-81), we obtain

$$A-\bar{n}B - H = a - h + \beta_{12}ha^2 \qquad (3\text{-}83)$$

Whence, solving the quadratic for a and combining with Eq.(3-75)

$$a = \frac{-1 + \sqrt{1 + 4\beta_{12}h\left[\frac{H-h}{\bar{n}_H} - (H-h)\right]}}{2\beta_{12}h} \qquad (3\text{-}84)$$

Values of a calculated from Eq.(3-84) give identical values to those obtained using Eq.(3-80) where the latter is a valid approximation.

In the copper mandelate system precipitation occurred at such low concentrations of A that dimeric and trimeric acid species did not have to be considered. Equations (3-76) and (3-80) were therefore valid in the whole range investigated.

3 - G - b) Formation of one complex.

The approach is similar to that in Sec. 2 - C - a where the

technique for finding the stability constant is described. When only one copper complex is formed Eq.(1-8) reduces to

$$\bar{n} = \frac{\beta_1 a}{1 + \beta_1 a} = \frac{a^*}{1 + a^*} \qquad (3\text{-}85)$$

where [cf. Eq.(3-16)]

$$\log a^* = \log a + \log \beta_1 \qquad (3\text{-}86)$$

In the position of best fit the value of β_1 is found by solving Eq.(3-86). When more than one complex is formed a fairly accurate value of β_1 can be obtained by fitting the data up to $\bar{n} = 0.2$ on to the theoretical one-complex curve.

3 - G - c) Formation of two complexes - Projection Strip Method.

A very convenient way of obtaining stability constants from the formation curve for systems which can be described by two parameters and two variables, one of which can be normalised, is by the projection strip method (Rossotti, Rossotti and Sillén 1956; and Rossotti and Rossotti 1959). When only the first two complexes are formed Eq.(1-8) reduces to

$$\bar{n} = \frac{\beta_1 a + 2\beta_2 a^2}{1 + \beta_1 a + \beta_2 a^2} \qquad (3\text{-}87)$$

which on rearrangement and division by $\beta_2^{\frac{1}{2}} a$ gives

$$\frac{\bar{n}}{(1-\bar{n})} \cdot \frac{1}{\beta_2^{\frac{1}{2}} a} - \frac{(2-\bar{n})}{(1-\bar{n})} \beta_2^{\frac{1}{2}} a = \beta_1 \beta_2^{-\frac{1}{2}} \qquad (3\text{-}88)$$

whence

$$\frac{\bar{n}}{(1-\bar{n})} \cdot \frac{1}{a^*} - \frac{(2-\bar{n})}{(1-\bar{n})} a^* = p^* \qquad (3\text{-}89)$$

where

$$a^* = a\beta_2^{\frac{1}{2}} \qquad (3\text{-}90)$$

Thus $\bar{n}$ is a function of the normalised variable a^* and the parameter

$$p^* = \beta_1 \beta_2^{-\frac{1}{2}} = (K_1/K_2)^{\frac{1}{2}} \qquad (3\text{-}91)$$

which fixes the shape of the formation curve $\bar{n}(\log a)$. The family of theoretical curves $\log p^*(\log a^*)_{\bar{n}}$ is calculated from Eq.(3-89) using a number of convenient values of $\bar{n}$. The data for this family of curves have been given by Rossotti and Rossotti (1959) and the curves are plotted in Fig(5-8).

The experimental formation curve and the $\log p^*(\log a^*)_{\bar{n}}$ curves are plotted using the same abscissa scale. For each value of $\bar{n}$ used to calculate the family of theoretical curves, the value of log a, together with the experimental uncertainty in this value, is marked off on the log a axis. This projection strip $(\log a)_{\bar{n}}$ is superimposed on the family of theoretical curves parallel to the log a^* axis, and in such a position that the best fit is obtained for all values of $\bar{n}$ used. The ordinate corresponding to the best position of fit gives the value of log p^*, and $-\frac{1}{2}\log \beta_2$ is obtained from the equation

$$\log a_o = -\tfrac{1}{2}\log \beta_2 \qquad (3\text{-}92)$$

where log a_o is the value of log a at log a* = 0[cf. Eq.(3-90)]. The maximum limits of error in log p* and $-\frac{1}{2}\log \beta_2$ are given by the permissible vertical and horizontal displacements respectively of the projection strip whilst allowing the calculated values of $(\log a^*)_{\bar{n}}$ to remain within the experimental uncertainty.

The stepwise formation constants are then obtained from Eqs.(3-91) and (3-92) in the forms

$$\log p^* = \tfrac{1}{2}\log K_1 - \tfrac{1}{2}\log K_2 \qquad (3\text{-}93)$$

$$-\log a_o = \tfrac{1}{2}\log K_1 + \tfrac{1}{2}\log K_2 \qquad (3\text{-}94)$$

An empirical method was used to find the errors in log K_1 and log K_2. Initially these errors were taken as the sum of the errors in log p* and log a_o. All the various combinations of the maximum and minimum values of log K_1 and log K_2 were then used to calculate the corresponding values of log p* and log a_o and it was found that half the latter were outside the range given by the best position of fit. On taking the error as half the sum of the errors in log p* and log a_o, and repeating the process the limiting values obtained for log p* and log a_o were almost exactly those found from the permissible shifts of the projection strip.

If within the range of free ligand concentration to which the experimental data refer there is a plateau at $\bar{n} = 1$, or if the formation curve does not extend beyond the point where it fits the one-complex theoretical curve, the projection strip will fit the normalised curves for $\bar{n} \leq 1.0$ for any value of log p* above a lower

limit, log p^*_{min}. The correct value of log β_1 is obtained from Eqs.(3-91) and (3-92) regardless of the value of p* chosen, and an upper limit for log β_2 may be calculated from the value of log p_{min}.

When this method is used to obtain β_1 and β_2 the corresponding theoretical curve is readily obtained. The positions of the log $p^*(\log a^*)_{\bar{n}}$ curves are marked off, at the appropiate values of $\bar{n}$, with the projection strip in the best position of fit. These points are then projected back to their ordinate positions.

3 - H. SUCCESSIVE EXTRAPOLATION - MORE THAN TWO COMPLEXES PRESENT.

When more than two complexes are present in a system the successive stability constants can be readily calculated from the experimental data $\bar{n}(a)$ by the method of successive extrapolations which has been described by Rossotti and Rossotti (1955; 1961a, p110).

Eq.(1-8) on rearrangement becomes

$$\sum_{0}^{N} (\bar{n}-n)\beta_n a^n = 0 \qquad (3\text{-}95)$$

which gives

$$\frac{\bar{n}}{(1-\bar{n})a} = \beta_1 + \beta_2 \frac{(2-\bar{n})}{(1-\bar{n})} a + \sum_{3}^{N} \frac{(n-\bar{n})}{(1-\bar{n})} \beta_n a^{n-1} \qquad (3\text{-}96)$$

Thus the plot of $\bar{n}/(1-\bar{n})a$ against $(2-\bar{n})a/(1-\bar{n})$ gives β_1 as intercept and β_2 as the limiting slope as $a \rightarrow 0$. Having found β_1 precisely

Eq.(3-95) is again rearranged to give

$$\frac{\bar{n} - (1-\bar{n})\beta_1 a}{(2-\bar{n})a^2} = \beta_2 + \beta_3 \frac{(3-\bar{n})a}{(2-\bar{n})} + \sum_4^N \frac{(n-\bar{n})}{(1-\bar{n})}\beta_n a^{n-1} \qquad (3\text{-}97)$$

β_2 is obtained as intercept and β_3 as the slope as $a \rightarrow 0$ of the plot of $[\bar{n} - (1-\bar{n})\beta_1 a]/(2-\bar{n})a^2$ against $(3-\bar{n})a/(2-\bar{n})$. If this line has no curvature no BA_4 is detectable and the successive extrapolations can be discontinued at this point. Taking the successive extrapolation one step further will give in such a case, a horizontal line. The errors in β_1 and β_2 are given by the permissible range of values of the intercepts and in β_3 by the limiting slopes of the plot.

When the stability constants for a system where N>2 have been determined the theoretical formation curve for the set of constants obtained is calculated from Eq.(1-8) and the experimental data compared with it. If the constants evaluated are those which best explain the data the curve and the experimental results should agree with high precision over the entire experimental range of $\bar{n}$ and log a.

3 - I) RELATIVE AMOUNTS OF SPECIES PRESENT IN COPPER SYSTEMS.

The fraction, α_c, of central metal ion in the form of the various mononuclear complexes is calculated from

$$\alpha_c = \frac{[BA_c]}{b + [BA] + [BA_2] + \cdots + [BA_N]} = \frac{\beta_c a^c}{1 + \beta_1 a + \beta_2 a^2 + \cdots + \beta_N a^N} \qquad (3\text{-}98)$$

and plotted as a function of log a.

Thus when n = 3, the greatest value encountered in the present work,

$$\alpha_0 = \frac{1}{1 + \beta_1 a + \beta_2 a^2 + \beta_3 a^3} \qquad (3\text{-}99)$$

$$\alpha_1 = \alpha_0 \beta_1 a, \quad \alpha_2 = \alpha_0 \beta_2 a^2, \quad \alpha_3 = \alpha_0 \beta_3 a^3 .$$

CHAPTER 4.

CARBOXYLIC ACID EQUILIBRIA.

This study of the self-association of carboxylic acids in aqueous solution arose from the observation that the potential of a glass electrode immersed in a sodium carboxylate-carboxylic acid buffer did not remain constant, but varied with the total carboxylate concentration. This effect could be caused by a variation in one or more of three terms contained in the expression [cf. Eq.(3-1).]

$$E. = E_o'. + Ej - 59.15 \log \gamma_H - 59.15 \log h = E_o - 59.15 \log h \quad (4\text{-}1)$$

a) A variation in the liquid junction potential between the solution (3.00M with respect to sodium and perchlorate ions) in the J piece of the salt bridge, and the solution (3.00M with respect to sodium and perchlorate plus carboxylate ions) in the titration vessel.

b) A variation in activity coefficients during the partial exchange of perchlorate ions with carboxylate ions.

c) A real variation in hydrogen ion concentration.

The first and second factors are not considered to be major causes of the variation in the potential for several reasons outlined below.

Henderson's approximate equation for the liquid junction potential has been put in the convenient form (4-2) by Buchi (1924)

$$E_j = -\frac{RT}{F} \cdot \frac{D^{11} - D^1}{S^{11} - S^1} \cdot \ln \frac{S^{11}}{S^1} \quad (4\text{-}2)$$

where $$D = (\sum c_i t_i)_{cations} - (\sum c_i t_i)_{anions}$$

$$S = (\sum c_i |z_i| t_i)_{cations} + (\sum c_i |z_i| t_i)_{anions}$$

$$= (\sum c_i t_i)_{cations} + (\sum c_i t_i)_{anions}$$

when $z_i = 1$

c_i = molar concentration.

t_i = ionic conductivity.

z_i = ionic charge.

The superscripts ^{1} and ^{11} refer to the solutions nearer the negative and positive poles of the cell respectively.

Therefore, for the cell (2-1) used in this work

$$D^{11} = 3t_{Na^+} - 3t_{ClO_4^-}$$

$$D^{1} = 3t_{Na^+} - (3-x)t_{ClO_4^-} - xt_{A^-}$$

$$S^{11} = 3t_{Na^+} + 3t_{ClO_4^-}$$

$$S^{1} = 3t_{Na^+} + (3-x)t_{ClO_4^-} + xt_{A^-}$$

where x = concentration of sodium carboxylate.

Terms in h can be neglected when $h < 10^{-3}M$.

At best Henderson's equation is only approximate and potentials calculated by it cannot be used to correct experimental results accurately. Furthermore, the values obtained for E_j using limiting conductivities are different in both magnitude and sign, from those obtained using conductivities appropriate to the concentrations of the constituents. It would seem to be more correct to use the

conductivities for real concentrations rather than limiting conductivities. The solutions where the ionic species differ most from a solution 3.00M with respect to perchlorate are those with $\bar{n} = 0.05$ and A = 1000mM. In such solutions the calculated liquid junction potentials are of the order of -2 to -3mV, using conductivities appropriate to the concentrations of the constituents. This corresponds to an experimentally observed change in potential of about +8mV, Thus, although there is a possibility of a liquid junction potential occurring, it appears to be of opposite sign to the observed potential change. In addition, the experimental potential change in a 3.00M sodium perchlorate medium is larger than Sundén(1953) and Sonesson(1958) found for a 2.00M medium, and larger still than Fronaeus(1948) and Ahrland(1951) found for a 1.00M medium. If the effect were caused by a liquid junction potential it would be expected to be smallest in a 3.00M sodium perchlorate medium and largest in 1.00M sodium perchlorate.

An approximate calculation based on Harned's rule (Martin 1961), and the fact that not only the magnitude, but also the sign, of the variation in potential depend on the salt:acid ratio of the buffers, indicate that the possibility of serious variation in the activity coefficients can be discounted. Such variation as there may be would cause a change in potential of the same order, but opposite in sign, to the possible liquid junction potential. If there were both a liquid junction potential and a variation in activity coefficients, the resultant changes in potential from these two effects would roughly cancel.

Therefore the observed variation in potential has been ascribed entirely to real variations in hydrogen ion concentration caused by polynuclear complex formation. This hypothesis has been pursued rigorously in terms of the law of mass action. The validity of this hypothesis appears to be justified by the good agreement obtained between the experimental and theoretical curves. [See Figs. 4-2, 4-4, 4-5, 4-7, 4-8, 4-10]. It is very unlikely that such good fits would have been obtained if the changes in potential had been caused by a junction potential and variation in the activity coefficients, as opposed to variation in the hydrogen ion concentration.

4 - A. RESULTS.

The titration procedure used has been described in Sec 2 - D - b. E_o was calculated as detailed in Sec 3 - A and h was obtained from the values of E using Eq.(3-2). Values of C_{HA} and A were known from the analytical composition of the buffer. Thereafter $\bar{n}$ was calculated by using Eq.(3-10). The full experimental data for a typical buffer are given in Table 4-1.

The experimental results for each system studied are summarised in the appendix at the end of this chapter. In the numerous instances when duplicate titrations were carried out the results were identical within the experimental error in E of $\pm$ 0.2mV. Therefore, only one set of such results has been recorded. These experimental results were used to plot $\bar{n}(\log h)_A$ curves for several values of A. Log $A(\log h)_{\bar{n}}$ curves were then prepared by reading off values of log h, for fixed values of $\bar{n}$, from the $\bar{n}(\log h)_A$ curves. These data are given in the text.

TABLE 4 - 1

Experimental data for a chloroacetic acid buffer titration.

Buffer composition: HA = 877 mM; A = 1751 mM. E_o = 266.0 mV

V_{Bu}	V_T	HA	A	E(mV)	$E-E_o$	pH	log h	h	C'_H	$\bar{n}$
0.00	19.05	-	-	274.0	8.0	3.135	$\bar{4}$.865	0.732	0.732	-
0.05	19.10	2.302	4.583	269.8	3.8	3.064	$\bar{4}$.936	0.863	0.731	0.474
0.10	19.15	4.581	9.14	268.6	2.6	3.044	$\bar{4}$.956	0.904	0.729	0.482
0.30	19.35	13.60	27.14	267.7	1.7	3.029	$\bar{4}$.971	0.936	0.721	0.493
0.55	19.60	24.62	49.12	267.4	1.4	3.024	$\bar{4}$.976	0.947	0.712	0.496
0.85	19.90	37.47	74.8	267.4	1.4	3.024	$\bar{4}$.976	0.947	0.701	0.498
1.15	20.20	49.94	99.7	267.4	1.4	3.024	$\bar{4}$.976	0.947	0.691	0.499
2.45	21.50	100.0	199.5	267.8	1.8	3.030	$\bar{4}$.970	0.932	0.649	0.500
3.95	23.00	150.7	300.7	268.3	2.3	3.039	$\bar{4}$.961	0.914	0.607	0.500
5.65	24.70	200.7	400.4	268.8	2.8	3.047	$\bar{4}$.953	0.897	0.565	0.500
7.60	26.65	250.2	499.2	269.2	3.2	3.054	$\bar{4}$.946	0.883	0.524	0.500
9.90	28.95	300.0	599	269.7	3.7	3.063	$\bar{4}$.937	0.866	0.482	0.501
12.65	31.70	350.1	699	270.1	4.1	3.069	$\bar{4}$.931	0.853	0.440	0.501
16.00	35.05	400.4	799	270.7	4.7	3.079	$\bar{4}$.921	0.833	0.398	0.501
20.10	39.15	450.4	899	271.2	5.2	3.088	$\bar{4}$.912	0.815	0.356	0.501
25.30	44.35	500.4	999	271.8	5.8	3.098	4.902	0.798	0.315	0.501

V_{Bu} = volume of buffer solution added. Volumes are given in ml., and concentrations in millimoles per litre.

FIG. 4-1 PHENYLACETIC ACID ○ Experimental points for A≤20mM.
——— Mononuclear formation curve.

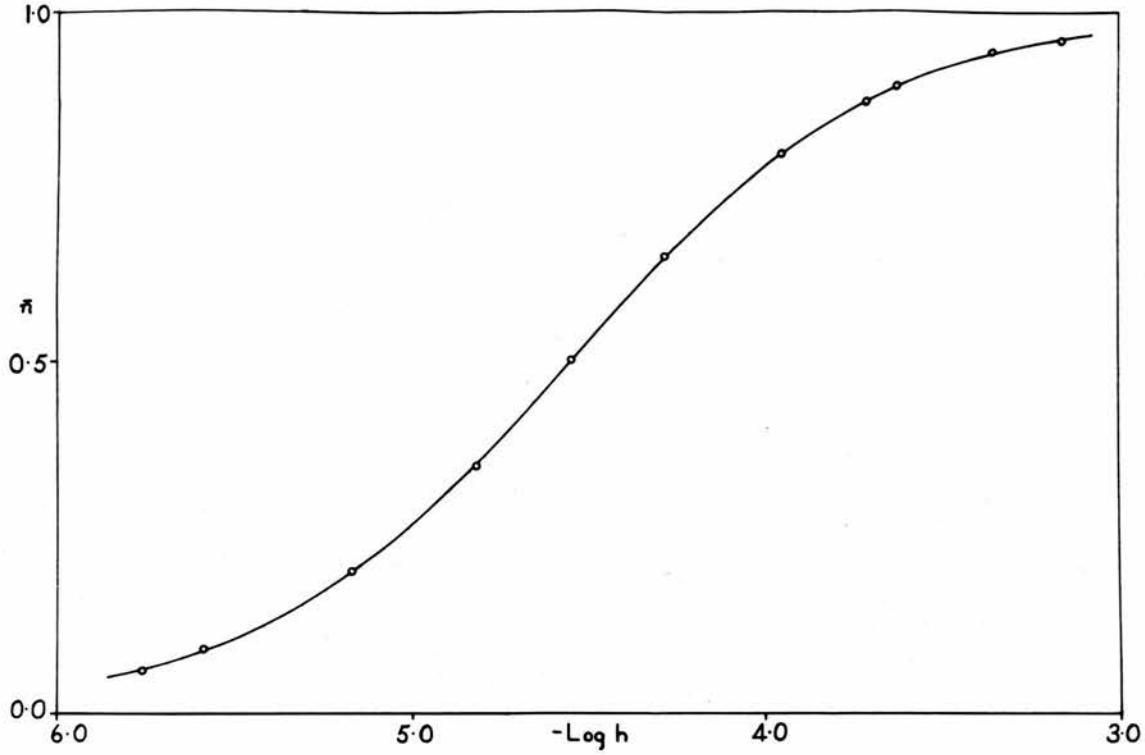
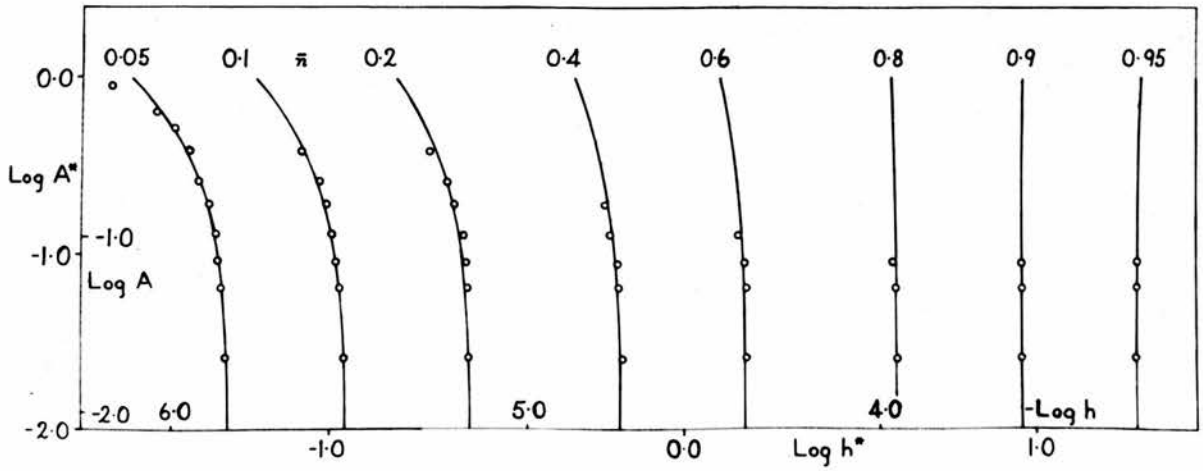


FIG. 4-2 PHENYLACETIC ACID ○ Experimental data log A(log h)$_{\bar{n}}$
——— Normalised log A*(log h*)$_{\bar{n}}$ R=0·45 curves calculated using Eq. (3-35)



The constants for each system were then obtained by curve-fitting, as described in Sec. 3-C.

4 - A - a. Phenylacetic acid.

The experimental results for phenylacetic acid are summarised in Table 4A-1. [The tables 4A-1 etc. appear in the appendix at the end of this chapter]. Formation curves were plotted for several values of A and compared with the theoretical mononuclear curve calculated using Eq.(3-15). The curve for A ≤ 20mM fitted the theoretical curve with high precision as shown in Fig. 4-1. A value of 4.556 ± 0.007 was obtained from this fit as described in Sec. 3 - C - a.

However, polynuclear association occurs at higher concentrations where the $\bar{n}(\log h)_A$ curves are functions of A. The presence of an isohydric point suggests that the polynuclear species may be of a common degree of condensation, but as the dependence on A is not very marked the polynuclear association is comparatively slight. As a working hypothesis, therefore, it was assumed that the polynuclear species were probably dinuclear. If HA and HA_2 were the only species formed in the system then the isohydric point would be precisely at $\bar{n} = 0.50$. If, on the other hand, the sole polynuclear species were the neutral dimer then the curves would be more nearly parallel and would coalesce at $\bar{n} = 1.0$. The hypothesis adopted therefore was that both the species HA_2 and H_2A_2 are formed in addition to HA.

Phenylacetic acid has an isohydric point at $\bar{n} = 0.909 \pm 0.025$ corresponding to a value of $0.45 \pm 0.01_5$ for R [Sec. 3 - C - b(ii)]. The experimental data $\log A(\log h)_{\bar{n}}$, given in Table 4-2 were compared

with the family of normalised log $A^*(\log h^*)_{\bar{n},R}$ curves calculated from Eq.(3-35) using R = 0.45, and placed in the position of best fit, as shown in Fig. 4-2.

Table 4-2.

Phenylacetic Acid : $A,(\log h)_{\bar{n}}$ data.

AmM \ $\bar{n}$	0.05	0.10	0.20	0.40	0.60	0.80	0.90	0.95
	pH	pH	pH	pH	pH	pH	pH	pH
≤20	5.852	5.521	5.172	4.736	4.379	3.959	3.601	3.282
50	5.869	5.537	5.174	4.740	4.381	3.964	3.601	3.279
70	5.876	5.546	5.180	4.749	4.390	3.970	3.602	3.277
100	5.882	5.554	5.186	4.769	4.411			
150	5.900	5.573	5.211	4.787				
200	5.933	5.594	5.234					
300	5.960	5.641	5.285					
400	5.000							
500	5.056							
700	5.179							

In the position of best fit when $(\log A^*, \log h^*) = (0,0)$ $(\log A, \log h) = (-0.10 \pm 0.02, -4.557 \pm 0.008)$. Whence, using Eqs.(3-25), (3-39), and (3-40)

$$\log \beta_{11} = 4.557 \pm 0.008$$

$$\log \beta_{12} = 4.66 \pm 0.03$$

$$\log \beta_{22} = 8.87 \pm 0.04$$

The step stability constants can now be evaluated using Eqs.(3-39a), (3-41), and (3-42). These values are

$$\log K_{12} = +0.10 \pm 0.02$$

$$\log K_{22} = 4.21 \pm 0.02$$

$$\log K_D = -0.25 \pm 0.04$$

FIG. 4-3 Formation curves for A ≤ 50mM and A=1000mM

---- ≤50mM —— 1000mM

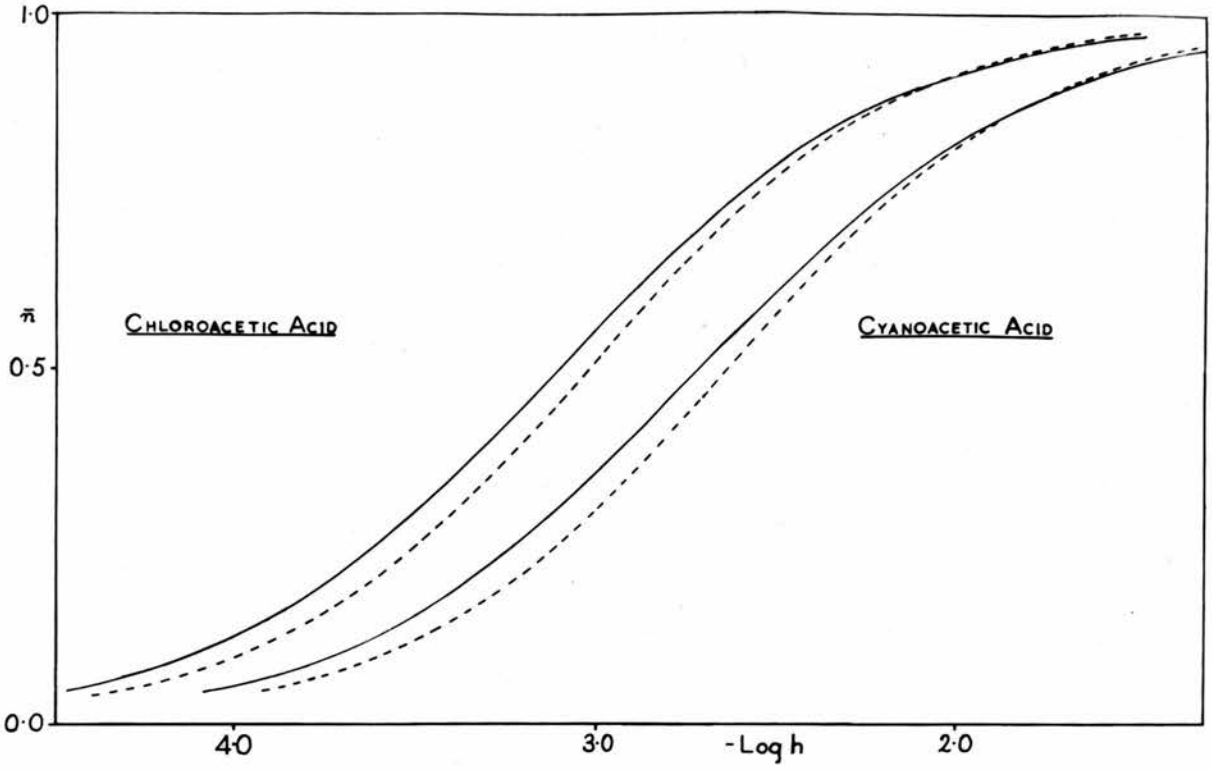
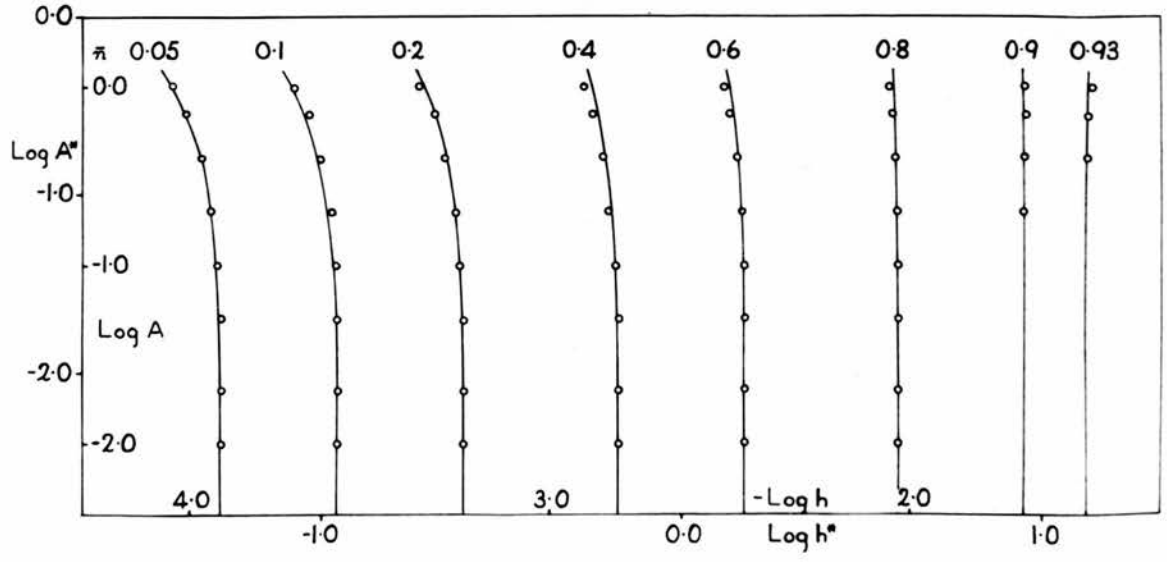


FIG. 4-4 CYANOACETIC ACID ○ Experimental data $\log A(\log h)_{\bar{n}}$

—— Normalised $\log A^*(\log h^*)_{\bar{n},R=0.425}$ curves calculated using Eq. (3-35).



The slight deviation of the experimental points from the theoretical curves at high concentrations of A is consistent with the formation of trinuclear species. Owing to the low solubility of the acid sufficient data could not be obtained to investigate this tendency quantitatively. An attempt was made to fit the experimental data to the combination of species HA, HA_2, H_2A_3 [Sec 3 - C - b(iii)] but the overall fit was less satisfactory.

4 - A - b. Cyanoacetic acid.

The experimental results for cyanoacetic acid are summarised in Tables 4A-2 and 4A-3, and the data A,$(\log h)_{\bar{n}}$ given in Table 4-3. Formation curves were drawn for A ≤ 50mM and A = 100, 200, 400, 700, 1000mM. Those for A ≤ 50mM and A = 1000mM are shown in Fig. 4-3.

Table 4-3.

Cyanoacetic Acid : A,$(\log h)_{\bar{n}}$ data.

AmM \ $\bar{n}$	0.05	0.10	0.20	0.40	0.60	0.80	0.90	0.93
	pH	pH	pH	pH	pH	pH	pH	pH
≤50	3.918	3.591	3.238	2.811	2.460	2.029		
100	3.929	3.594	3.249	2.821	2.461	2.030		
200	3.943	3.602	3.260	2.839	2.469	2.033	1.682	
400	3.969	3.639	3.290	2.853	2.480	2.038	1.681	1.507
700	4.010	3.668	3.325	2.880	2.501	2.045	1.679	1.503
1000	4.051	3.709	3.358	2.908	2.517	2.056	1.672	1.492

The exact coincidence of the formation curve for A ≤ 50mM with the normalised curve for one complex suggests that this system is mononuclear for A ≤ 50mM. From Eqn.(3-16) $\log \beta_{11} = 2.634 \pm 0.005$.

Again the presence of a sharp isohydric point and the relatively slight dependence of $\bar{n}(\log h)_A$ plots on A suggested that the results

could be interpreted by assuming the presence of the dinuclear species HA_2 and H_2A_2. The isohydric point occurs at $\bar{n} = 0.870 \pm 0.010$ corresponding to $R = 0.42_5 \pm 0.01$ [Eq.(3-38)]. The experimental data log A,$(\log h)_{\bar{n}}$ were compared with the family of log A*$(\log h^*)_{\bar{n},R}$ curves calculated using Eq.(3-35) with $R = 0.42_5$, and the position of best fit is shown in Fig. 4-4.

In the position of best fit when (log A*,log h*) = (0,0) (log A,log h) = $(0.40 \pm 0.02, -2.634 \pm 0.005)$. The values of the various equilibrium constants obtained from Eqs.(3-25), (3-39), (3-40), (3-39a), (3-41), and (3-42) are

$\log \beta_{11} = 2.634 \pm 0.005$ $\qquad$ $\log K_{12} = -0.40 \pm 0.02$

$\log \beta_{12} = 2.23 \pm 0.02_5$ $\qquad$ $\log K_{22} = 2.26 \pm 0.01_5$

$\log \beta_{22} = 4.50 \pm 0.03_5$ $\qquad$ $\log K_D = -0.77 \pm 0.03$

The deviation of some of the data at A ≥ 700mM from the normalised curves is consistent with the formation of a small amount of trimeric species. As the deviation is only very slight it was considered that calculation of further stability constants would be attempting to obtain more information than was justified from the results.

4 - A - c. Chloroacetic acid.

The experimental results for chloroacetic acid are summarised in Tables 4A-4 and 4A-5, and the data A,$(\log h)_{\bar{n}}$ are given in Table 4-4. This system was also found to be mononuclear for A ≤ 50mM, and comparison of the formation curve for this concentration with the normalised curve for one complex gave a value of 3.018 ± 0.005 for

FIG. 4-5 CHLOROACETIC ACID ○ Experimental data $\log A(\log h)_{\bar{n}}$
—— Normalised $\log A^{n}(\log h^{*})_{\bar{n}.R=0.45}$ curves calculated using Eq. (3-35)

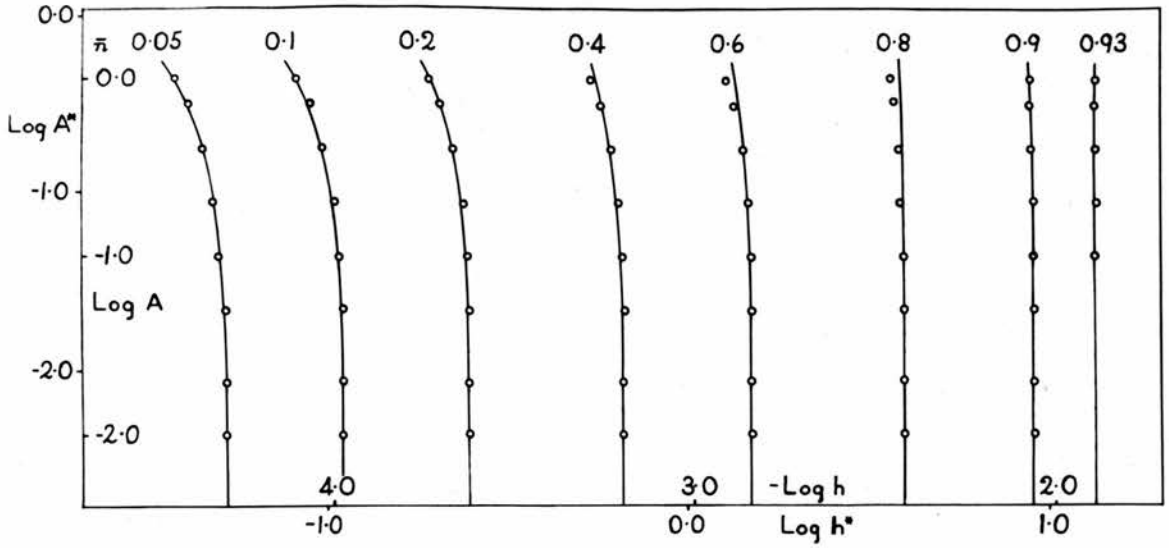
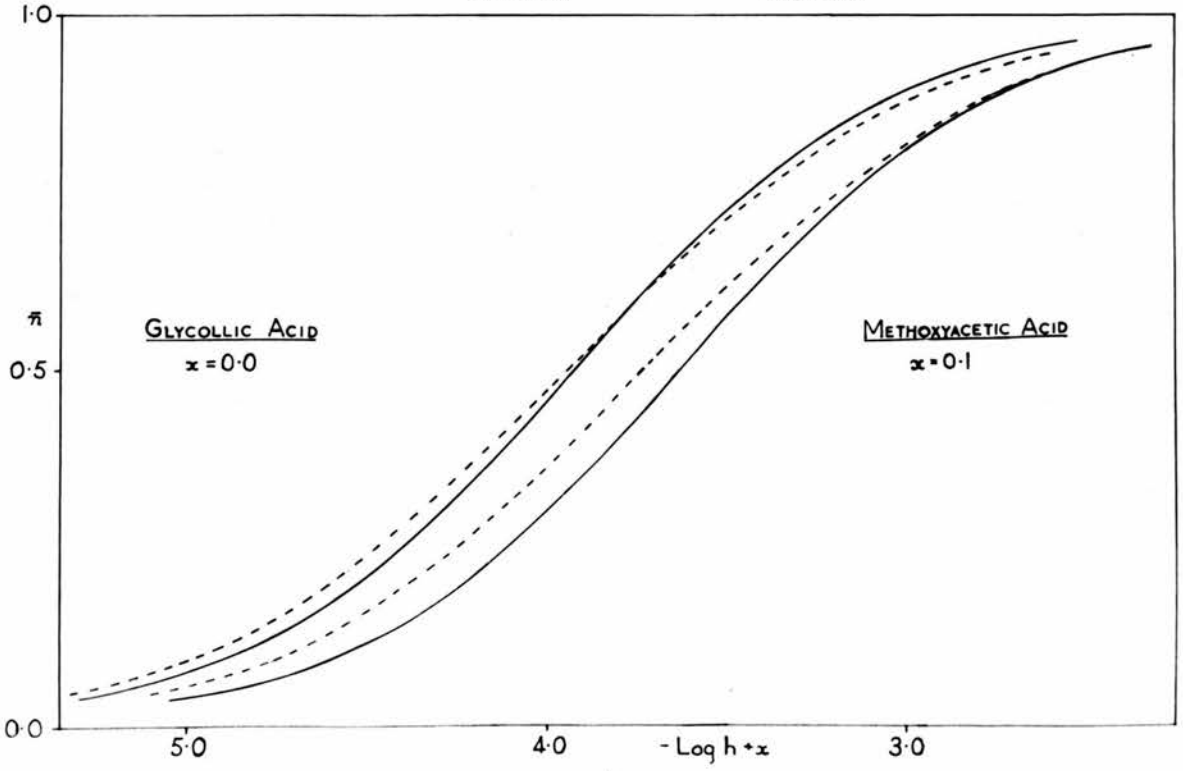


FIG. 4-6 Formation curves for A ≤ 50mM and A=1000mM
——≤ 50mM - - - - 1000mM



$\log \beta_{11}$. At higher concentrations the behaviour was similar to that already observed in cyanoacetic acid, and the results were analysed accordingly. The formation curves for A ≤ 50mM and A = 1000mM are shown in Fig. 4-3. An isohydric point occurs at $\bar{n} = 0.910 \pm 0.010$ giving $R = 0.45 \pm 0.01$. The experimental data $\log A(\log h)_{\bar{n}}$ were compared with the family of $(\log A^*, \log h^*)_{\bar{n},R}$ curves calculated from Eq.(3-35) using R = 0.45, and placed in the position of best fit as shown in Fig. 4-5. In this position, when $(\log A^*, \log h^*) = (0,0)$, $(\log A, \log h) = (0.36 \pm 0,02, -3.018 \pm 0.005)$

Table 4-4.

Chloroacetic Acid : $A,(\log h)_{\bar{n}}$ data.

AmM \ $\bar{n}$	0.05	0.10	0.20	0.40	0.60	0.80	0.90	0.93
	pH	pH	pH	pH	pH	pH	pH	pH
≤50	4.302	3.974	3.621	3.294	2.840	2.419	2.059	
100	4.322	3.986	3.632	3.300	2.842	2.421	2.059	1.889
200	4.339	4.000	3.641	3.312	2.847	2.429	2.059	1.884
400	4.360	4.034	3.666	3.329	2.863	2.436	2.063	1.881
700	4.403	4.068	3.703	3.360	2.889	2.448	2.068	1.884
1000	4.442	4.110	3.739	3.389	2.911	2.458	2.068	1.881

The values of the stability constants obtained from Eqs.(3-25), (3-39), (3-40), (3-39a), (3-41), and (3-42) are

$\log \beta_{11} = 3.018 \pm 0.005$ $\log K_{12} = -0.36 \pm 0.02$

$\log \beta_{12} = 2.66 \pm 0.02_5$ $\log K_{22} = 2.67 \pm 0.01_5$

$\log \beta_{22} = 5.33 \pm 0.03_5$ $\log K_D = -0.71 \pm 0.03$

Some slight deviations at concentrations ≥ 700mM, similar to those in the cyanoacetate system, occur in this system also, but again too few data are available to justify calculating constants for trimeric species.

4 - A - d. Glycollic acid.

A summary of the experimental results for glycollic acid is given in Tables 4A-6 and 4A-7, and the data $A,(\log h)_{\bar{n}}$ are given in Table 4-5. The formation curve for A ≤ 50mM coincides with the theoretical mononuclear curve with high precision, showing that this system is mononuclear in the range A ≤ 50mM. A value of 3.920 ± 0.005 was obtained for $\log \beta_{11}$ from Eq.(3-16).

Table 4-5.

Glycollic Acid : $A,(\log h)_{\bar{n}}$ data.

AmM \ $\bar{n}$	0.05	0.10	0.20	0.40	0.60	0.80	0.90	0.95
	pH	pH	pH	pH	pH	pH	pH	pH
≤50	5.202	4.869	4.523	4.096	3.747	3.321	2.968	2.640
100	5.219	4.877	4.526	4.101	3.747	3.314	2.964	2.646
200	5.226	4.885	4.533	4.107	3.745	3.309	2.958	2.631
400	5.244	4.909	4.550	4.111	3.742	3.300	2.941	2.613
700	5.273	4.937	4.575	4.125	3.745	3.288	2.922	2.596
1000	5.298	4.968	4.599	4.138	3.746	3.273	2.900	2.570

At higher concentrations the $\bar{n}(\log h)_A$ curves are functions of A. A sharp isohydric point occurs at $\bar{n} = 0.605 \pm 0.010$ as seen from Fig. 4-6 where the formation curves for A ≤ 50mM and A = 1000mM are drawn. The working hypothesis adopted was that the species HA, HA_2, and H_2A_2 are formed, and the experimental data $\log A(\log h)_{\bar{n}}$ were compared with the family of $\log A^*(\log h^*)_{\bar{n},R}$ curves calculated using Eq.(3-35) with R = 0.174. Up to the limit of the experimental measurements there is very close agreement between the normalised curves

FIG. 4-7 GLYCOLLIC ACID ○ Experimental data $\log A(\log h)_{\pi}$
—— Normalised $\log A^*(\log h^*)_{\pi,R=0.174}$ curves calculated using Eq. (3-35)

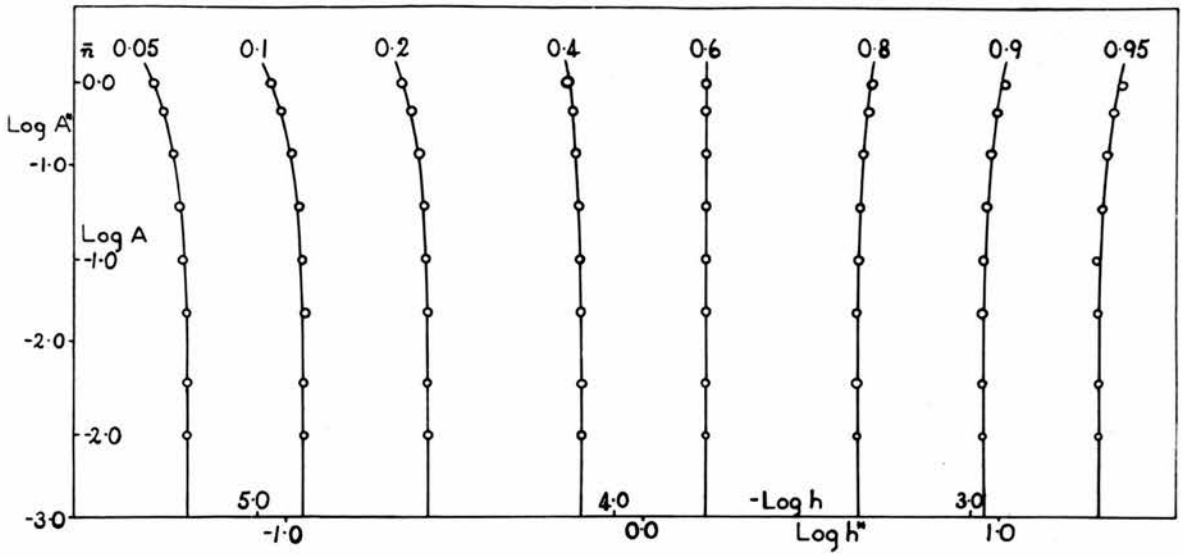
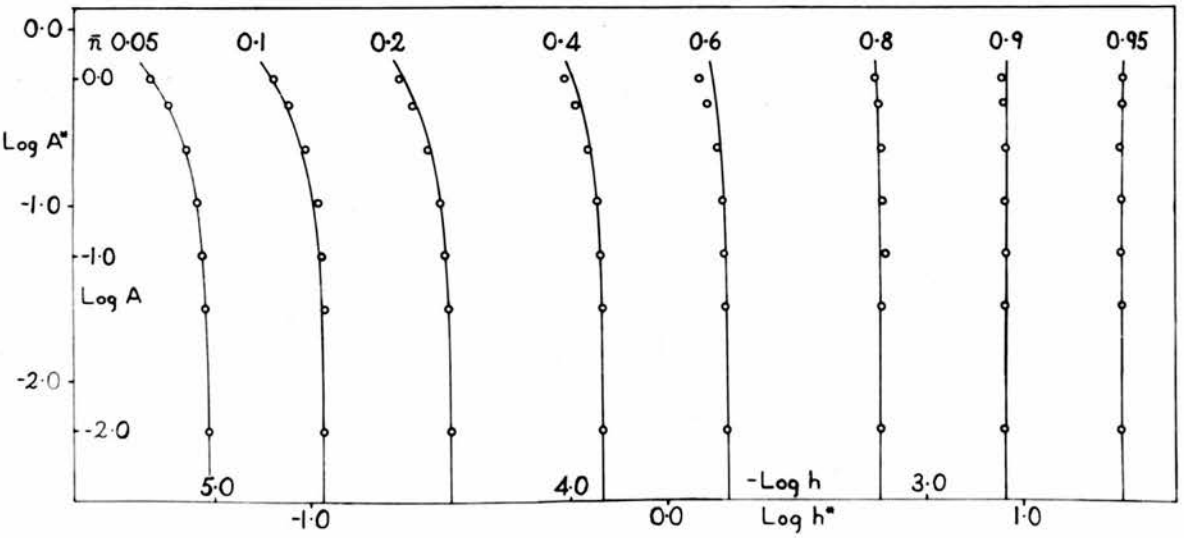


FIG. 4-8 METHOXYACETIC ACID ○ Experimental data $\log A(\log h)_{\pi}$
—— Normalised $\log A^*(\log h)_{\pi,R=0.462}$ curves calculated using Eq. (3-35)



and the experimental data, as shown in Fig. (4-7).

In the position of best fit (log A,log h) = (0.53 ± 0.02, -3.920 ± 0.005) when (log A*,log h*) = (0,0). Whence, using Eqs.(3-25), (3-39), (3-40), (3-39a), (3-41) and (3-42)

$\log \beta_{11} = 3.920 \pm 0.005$ $\log K_{12} = -0.53 \pm 0.02$

$\log \beta_{12} = 3.39 \pm 0.02_5$ $\log K_{22} = 3.16 \pm 0.04$

$\log \beta_{22} = 6.55 \pm 0.06_5$ $\log K_D = -1.29 \pm 0.06$

4 - A - e. Methoxyacetic Acid.

Tables 4A-8 and 4A-9 contain a summary of the experimental results for methoxyacetic acid. The data A,$(\log h)_{\bar{n}}$ are given in Table 4-6.

Table 4-6.

Methoxyacetic Acid : A,$(\log h)_{\bar{n}}$ data.

AmM \ $\bar{n}$	0.05	0.10	0.20	0.40	0.60	0.80	0.90	0.95
	pH	pH	pH	pH	pH	pH	pH	pH
≤50	5.019	4.689	4.337	3.910	3.559	3.128	2.779	2.451
100	5.037	4.698	4.356	3.919	3.570	3.118	2.779	2.450
200	5.051	4.711	4.370	3.931	3.576	3.122	2.779	2.450
400	5.081	4.744	4.403	3.955	3.592	3.131	2.781	2.454
700	5.134	4.792	4.448	3.992	3.620	3.142	2.785	2.449
1000	5.183	4.836	4.489	4.023	3.640	3.150	2.790	2.446

This system was found to be similar to all the previous systems studied, and the hypothesis that HA, HA_2, and H_2A_2 are formed appeared to be valid in this case also. As before formation curves were drawn for several values of A, and it was found that the system was mononuclear in

the range $A \leq 50mM$, where $\bar{n}(\log h)$ is independent of A. A value of 3.728 ± 0.005 was obtained for $\log \beta_{11}$ from Eq.(3-16).

The formation curves for $A \leq 50mM$ and $A = 1000mM$, shown in Fig. 4-6, indicate the isohydric point at $n = 0.930 \pm 0.025$, giving a value of 0.462 ± 0.014 for R. This value of R was used to calculate a family of normalised $\log A^*(\log h^*)_{\bar{n},R}$ curves with which to compare the experimental data $\log A(\log h)_{\bar{n}}$. The good agreement between the normalised curves and the experimental data (Fig. 4-8) supports the hypothesis adopted.

In the best position of fit (log A, log h) = $(0.28 \pm 0.02, -3.728 \pm 0.005)$ when (log A*, log h*) = (0,0). The equilibrium constants were evaluated in the usual way, the values obtained being

$\log \beta_{11} = 3.728 \pm 0.005$ $\qquad$ $\log K_{12} = -0.28 \pm 0.02$

$\log \beta_{12} = 3.45 \pm 0.02_5$ $\qquad$ $\log K_{22} = 3.39 \pm 0.02$

$\log \beta_{22} = 6.84 \pm 0.04$ $\qquad$ $\log K_D = -0.62 \pm 0.03$

This is yet another system where slight trimeric formation is suggested by the small divergence of some of the experimental data from the normalised curves, when $A \geq 700mM$. However, for the reasons given above no attempt has been made to compute stability constants.

4 - A - f. Phenoxyacetic Acid.

As the solubility of phenoxyacetic acid in 3.00M sodium perchlorate is only approximately 40mM per litre it was not possible to carry out buffer titrations at sufficiently high concentrations to investigate the self association of this acid. All the results from the previous

FIG. 4 - 9 PHENOXYACETIC ACID ○ Experimental points.
—— Mononuclear formation curve.

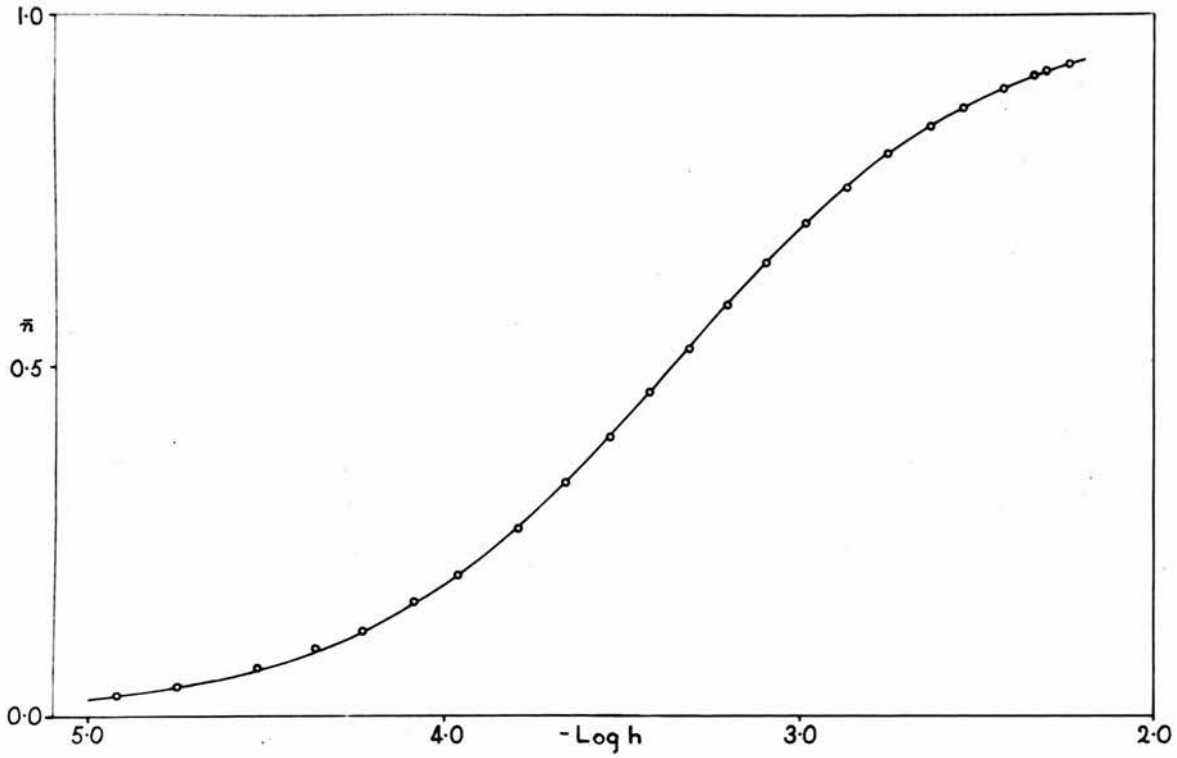
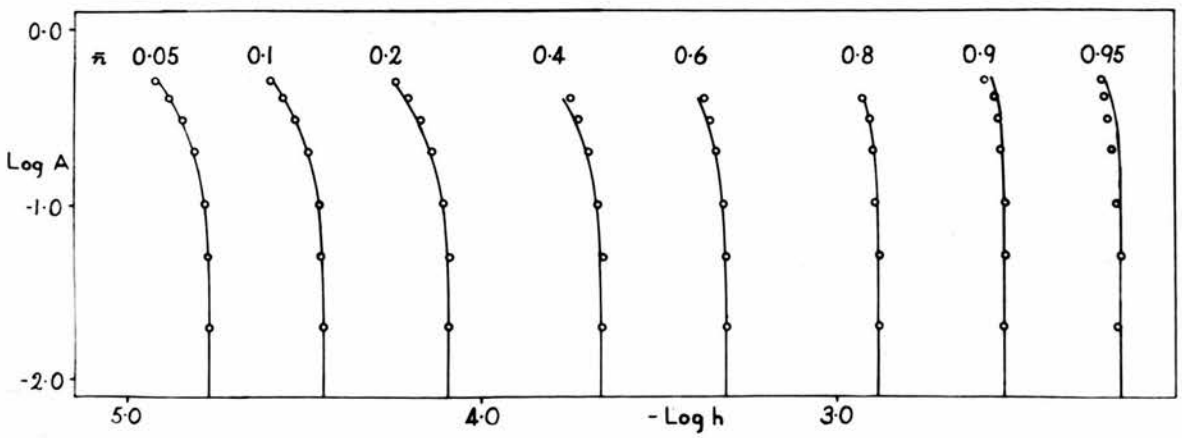


FIG. 4 - 10 MANDELIC ACID ○ Experimental data log A (log h)$_{\bar{n}}$
—— Curves calculated using the constants obtained in Sec. 4-A-g.



investigations have shown that only mononuclear species are formed when $A \lesssim 35mM$. (The figure of 50mM is too high when Clarke's(1960) work on the valerate, isobutyrate, and trimethylacetate systems is included). Therefore, it seemed highly likely that the formation curve obtained by titrating a solution of phenoxyacetic acid with sodium hydroxide would be identical to the normalised curve for one complex, HA, if A did not exceed ~20mM during the titration. The details of the experimental procedure used have been given in Sec 2 - D -d

The results of one of the titrations are given in Table 4A-10. A duplicate gave identical results. The detailed calculation of $\bar{n}$ is slightly different in this instance since a solution of phenoxyacetic acid is being neutralised gradually with sodium hydroxide. Thus we extend Eq.(3-10) to

$$\bar{n} = (A + C'_H - C_B - h)/A \qquad (4-3)$$

where C_B = concentration of sodium hydroxide at the point in question. The other symbols have been defined already. Figure 4-9 shows the close agreement between the experimental results and the theoretical curve for the formation of one complex. The value of $\log \beta_{11}$ obtained from Eq.(3-16) is 3.358 ± 0.005.

4 - A - g. Mandelic Acid.

The experimental results for mandelic acid are summarised in Tables 4A-11, 4A-12, and 4A-13. Those in Table 4A-13 are the results from triplicate titrations at A ~ 20mM, similar to the phenoxyacetic acid titrations, but the total mandelate concentration was held constant by adding 0.10ml. of 100mM mandelic acid solution for every

0.40ml. sodium hydroxide solution added. These titrations were carried out to obtain additional data at low values of A because some of the results from the buffer titrations were unreliable at low concentrations. This was due to the large error which could arise when adding small volumes of the perchloric acid solutions. The data for A $\leq$ 50mM agree closely with the theoretical curve for the formation of one complex and log β_{11} = 3.488. [Eq.(3-16)].

Table 4-7.

Mandelic Acid : A,(log h)$_{\bar{n}}$ data.

$\bar{n}$ / AmM	0.05	0.10	0.20	0.40	0.60	0.80	0.90	0.95
	pH	pH	pH	pH	pH	pH	pH	pH
≤20	4.770	4.445	4.089	3.663	3.310	2.882	2.533	2.212
50	4.773	4.457	4.090	3.661	3.312	2.882	2.528	2.202
100	4.784	4.460	4.109	3.674	3.319	2.891	2.527	2.214
200	4.814	4.492	4.140	3.702	3.342	2.899	2.540	2.227
300	4.850	4.532	4.173	3.730	3.363	2.911	2.548	2.235
400	4.887	4.566	4.209	3.758	3.381	2.929	2.560	2.248
500	4.927	4.600	4.242				2.583	2.249

Table 4-7 contains the data A,(log h)$_{\bar{n}}$. The results for A>50mM could not be explained in terms of the formation of HA, HA_2, and H_2A_2 only, and the hypothesis was extended to include the formation of the trinuclear species H_2A_3 and H_3A_3. The validity of this extension was checked by calculating $\bar{p}_{poly}$ and $\bar{q}_{poly}$ [Sec 3-D] for A = 400mM and the results are given in Table 4-8.

Table 4-8.

Calculation of $\bar{p}_{poly}$ and $\bar{q}_{poly}$ for A = 400mM in mandelate system.

pH	$\bar{n}$	$\bar{n}_1$	$\left(\frac{\partial \bar{n}}{\partial \ln A}\right)_h$	A_1 mM	$\bar{r}$	$\bar{p}_{poly}$	$\bar{q}_{poly}$
6.5	0.001	0.0009	0.0008				
6.1	0.003	0.0025	0.0020				
5.8	0.0055	0.005	0.0040				
5.4	0.015	0.011	0.0040				
5.0	0.039	0.032	0.0120	391.8	0.988	1.26	2.44
4.8	0.0595	0.047	0.0199	387.4	0.981	1.13	2.54
4.6	0.092	0.0705	0.0279	380.10	0.971	1.23	2.46
4.4	0.1385	0.1095	0.0398	369.9	0.956	1.19	2.41
4.2	0.203	0.164	0.0438	357.0	0.937	1.28	2.43
4.0	0.286	0.2345	0.0517	341.8	0.913	1.45	2.47
3.8	0.378	0.3285	0.0637	324.8	0.886	1.50	2.54
3.6	0.4835	0.434	0.0637	308.0	0.856	1.74	2.69
3.4	0.591	0.550	0.0517	293.8	0.829	1.98	2.81
3.2	0.6925	0.659	0.0338	283.1	0.808	2.26	2.92
3.0	0.776	0.753	0.0298	275.2	0.792	2.48	3.00
2.8	0.842	0.8295	0.0219	269.8	0.781	2.66	3.06
2.6	0.894	0.885	0.0080	266.5	0.775	2.80	3.07
2.4	0.9305	0.925	0.0020	264.6	0.772	2.88	3.06

An attempt was made to evaluate β_{12} and β_{22} by fitting normalised curves calculated using Eq.(3-53). Fits were possible using sets of curves with rather wide limits of R. The methods detailed in Sec. 3 - E - a were therefore used to obtain the stability constants.

The data for A $\leq$ 200mM were compared with a number of families of log A*(log h*)$_{\bar{n},R}$ curves for the combination of species HA, HA_2 H_2A_2 and the complete data for $\bar{n} \leq 0.3$ were simultaneously compared with sets of log A*(log h*)$_{\bar{n},R}$ curves for the combination of species HA, HA_2, and H_2A_3. The value found for log β_{12} was 3.29 ± 0.03. This value was then used to calculate β_{23} from Eqs.(3-63) and (3-65) using experimental

data for $\bar{n} \leq 0.3$ and A $\geq$ 100mM. Corresponding values of a and β_{23} were most readily found by successive approximations. Values of β_{12} and β_{23} were also determined by applying Eq.(3-69) to the complete range of experimental results using values of a obtained by graphical integration. Both methods gave the same values for the stability constants, i.e.

$$\log \beta_{12} = 3.29 \pm 0.03 \qquad \log \beta_{23} = 7.7_3 \pm 0.1$$

These values were employed in the calculation of β_{22} and β_{33} from the results for $\bar{n} \geq 0.6$ and A $\geq$ 100mM. Equation (3-65) was used to obtain values of a, and β_{22} and β_{33} were determined from Eq.(3-68). The intercept and slope of the resulting line gave,

$$\log \beta_{22} = 5.87_5 \pm 0.03 \qquad \log \beta_{33} = 10.8 \pm 0.1$$

respectively.

A check that the above values of the stability constants were a valid interpretation of the complete range of experimental measurements was made by calculating formation curves for A = 100, 200, 400, and (where applicable) 500mM. [Sec 3 - E - b]. There was close agreement between the experimental and calculated curves. The agreement is more readily seen when the data are plotted as log A$(\log h)_{\bar{n}}$ curves, see Fig. 4-10.

Stepwise constants for this system were evaluated from the overall stability constants. Values of the step stability constants K_{12}, K_{22}, and K_D were calculated from Eqs.(3-39a), (3-41), and (3-42).

$$\log K_{12} = -0.20 \pm 0.03_5$$

$$\log K_{22} = 2.59 \pm 0.06$$

$$\log K_D = -1.10 \pm 0.04$$

The other stepwise constants, defined by Eqs.(1-20) to (1-24) are given by

$$\log K_{23} = \log(\beta_{23}/\beta_{22}) = 1.86 \pm 0.14 \qquad (4\text{-}4)$$

$$\log K_{33} = \log(\beta_{33}/\beta_{23}) = 3.1 \pm 0.2 \qquad (4\text{-}5)$$

$$\log K_{DT} = \log(\beta_{33}/\beta_{11}\beta_{22}) = 1.44 \pm 0.14 \qquad (4\text{-}6)$$

$$\log K'_{23} = \log(\beta_{23}/\beta_{11}\beta_{12}) = 0.95 \pm 0.14 \qquad (4\text{-}7)$$

$$\log K_T = \log(\beta_{33}/\beta_{11}^3) = 0.34 \pm 0.12 \qquad (4\text{-}8)$$

4 - B. DISCUSSION.

The values of the stepwise equilibrium constants obtained in the present investigations are collected in Table 4-9, together with the equilibrium constants for the unsubstituted acids studied by Clarke(1960) and Martin(1961). Limits of error have been given in the appropiate preceding sections. In addition to the dimeric and trimeric species, for which the stability constants have been given, H_3A_4, H_4A_4, and yet larger species appear to be formed in the valerate, isobutyrate, and trimethylacetate systems at concentrations where micelle formation is not apparent.

The relative proportions of A in the form H_pA_q, α_{pq}, at A = 700mM in the cyanoacetate, chloroacetate, glycollate, and methoxyacetate systems, and at A = 400mM in the mandelate system, have been calculated as described in Sec 3-F. In the mandelate system A = 400mM was the

TABLE 4 - 9

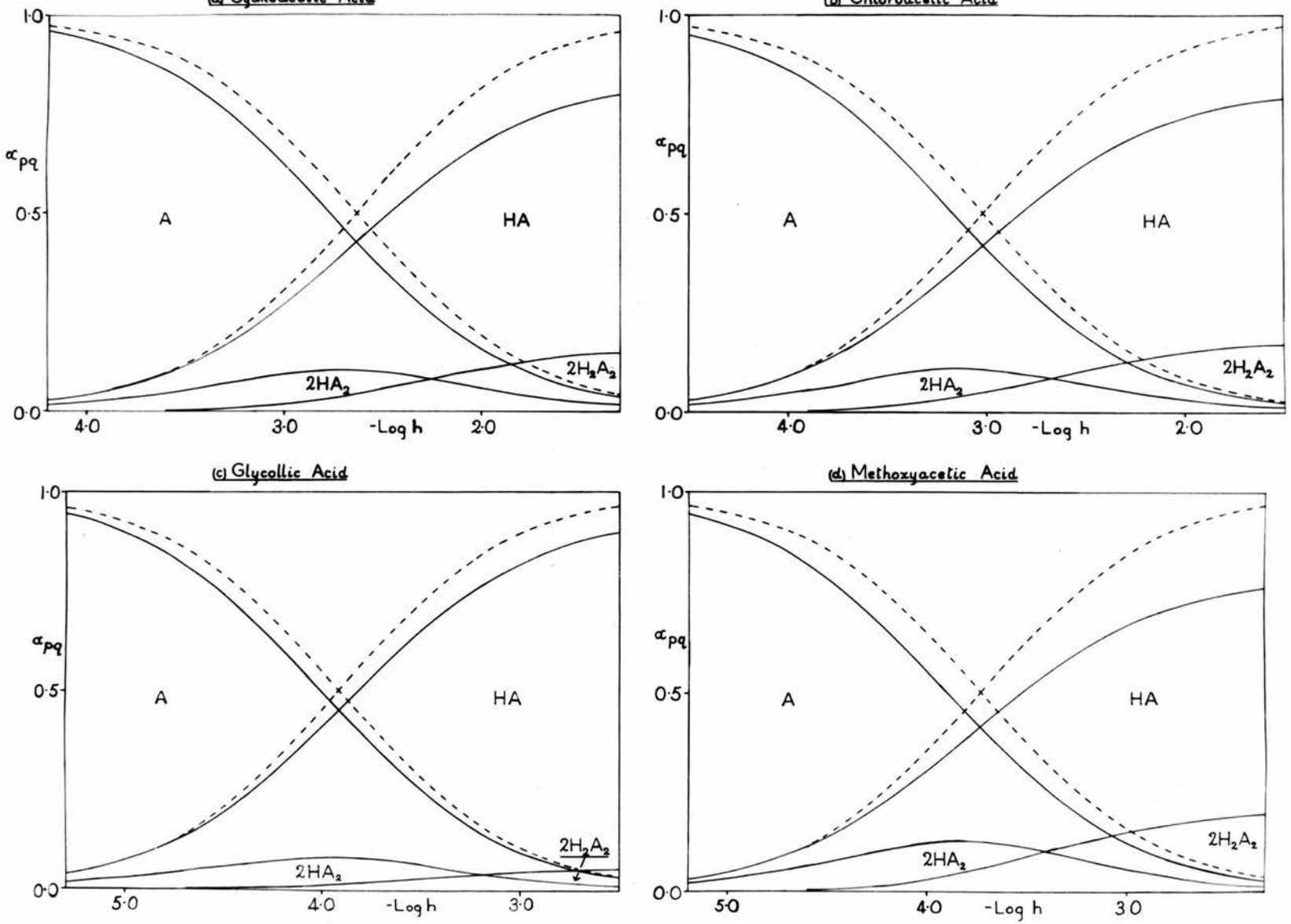
Proton - Carboxylate Association Constants in a 3.00 M Sodium (perchlorate)

Ionic Medium at 25.00 ± 0.05°C.

Acid	log K_{11}	log K_{12}	log K_{22}	log K_D	log R	log K_{23}	log K_{33}	log K_T	log K_{DT}	log K'_{23}
Formic *	3.900	-0.50	3.16	-1.24	-0.74					
Acetic *	5.014	-0.34	4.63	-0.73	-0.38					
Propionic*	5.161	-0.35	5.01	-0.50	-0.15	0.0	4.7	-1.0	-0.48	0.03
Butyric *	5.132	-0.24	5.11	-0.26	-0.02	+0.2	4.8	-0.4	-0.13	0.18
Valeric **	5.165	-0.10	5.17	-0.10	0.0	-0.14	5.20	-0.22	-0.14	-0.14
Isobutyric **	5.150	-0.27	5.15	-0.27	0.0	-0.27	5.15	-0.54	-0.27	-0.27
Trimethylacetic**	5.325	-0.14	5.33	-0.14	0.0	-0.18	5.23	-0.33	-0.18	-0.18
Cyanoacetic	2.634	-0.40	2.26	-0.77	-0.37					
Chloroacetic	3.018	-0.36	2.67	-0.71	-0.35					
Methoxyacetic	3.728	-0.28	3.39	-0.62	-0.33					
Phenylacetic	4.557	+0.10	4.21	-0.25	-0.35					
Glycollic	3.920	-0.53	3.16	-1.29	-0.76					
Mandelic	3.488	-0.20	2.59	-1.10	-0.90	1.86	3.1	+0.34	1.44	0.95

* Martin (1961) ** Clarke (1960)

FIG. 4-11 Relative proportions of A in the form H_pA_q in solutions of carboxylic acids at A = 700mM.



maximum concentration at which measurements were made over the entire pH range investigated. The results of these calculations are given in graphical form in Figs. 4-11 and 4-12 in which the dotted lines show the proportions at A ≤ 50mM when only the mononuclear species A and HA are present. These distribution curves show that the maximum amount of A in the form HA_2 when A = 700mM in the cyanoacetate, chloroacetate, glycollate, and methoxyacetate systems, is around 10% at a pH of approximately log K_{11} + 0.1. This was found in the unsubstituted acids also.

The proportion of the dimer H_2A_2, which is not formed in appreciable amounts at pH's above log K_{11} + 0.5, increases steadily with decrease in pH to the limit of the measurements. At those pH's the values of α_{22} for 700mM solutions of the substituted acids vary only slightly from that for acetic acid (~17%), except for glycollic acid where the amount is similar to that present in formic acid (~6%). These effects are caused by similarity in the values of K_D, K_{12}, and R for the corresponding systems. In strongly acidic solution

$$\alpha_{22} \approx \frac{2[H_2A_2]}{[HA] + 2[H_2A_2]} = \frac{2K_D[HA]}{1 + 2K_D[HA]}$$

$$= \frac{2RK_{12}[HA]}{1 + 2RK_{12}[HA]} \qquad (4\text{-}9)$$

On the other hand the amount of A in the form of H_2A_2 continues to increase from 17% in the acetate system, to 25% in the propionate and 33% in the butyrate system. When α_{22} has reached its maximum value

FIG. 4-12 Mandelic Acid Relative proportions of A in the form H_pA_q in solution at A = 400m M

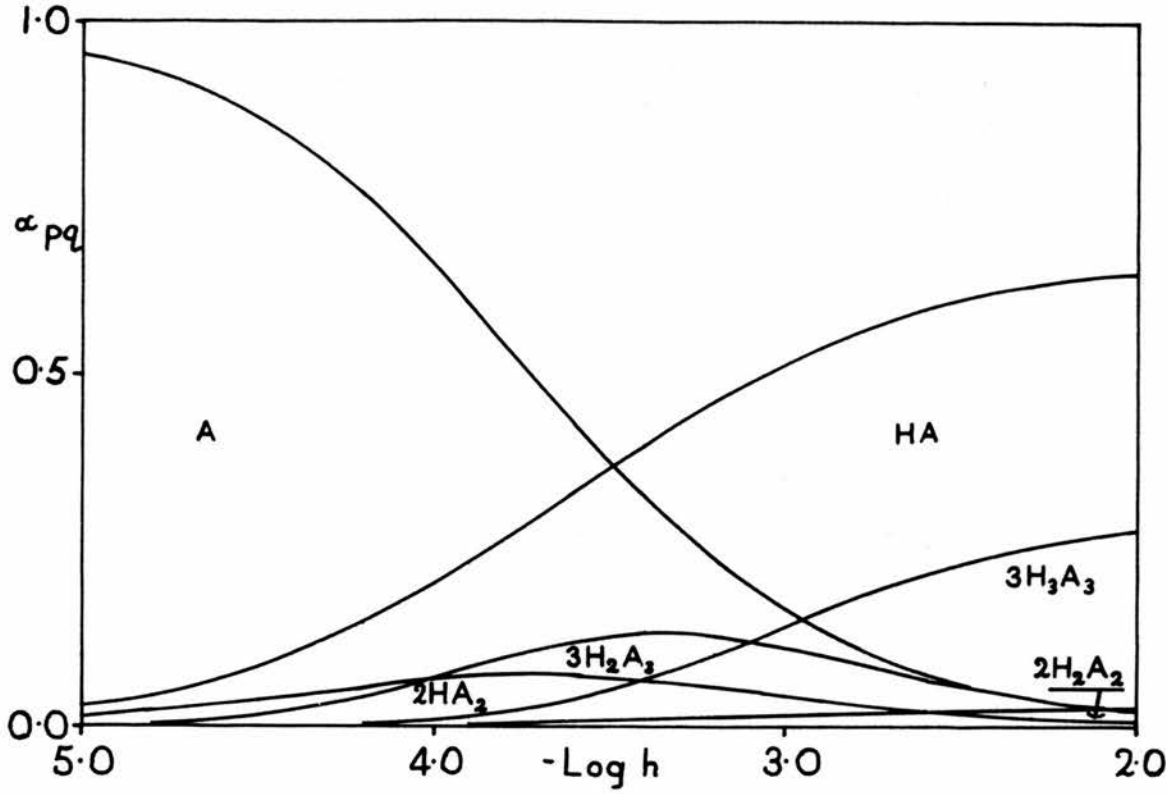
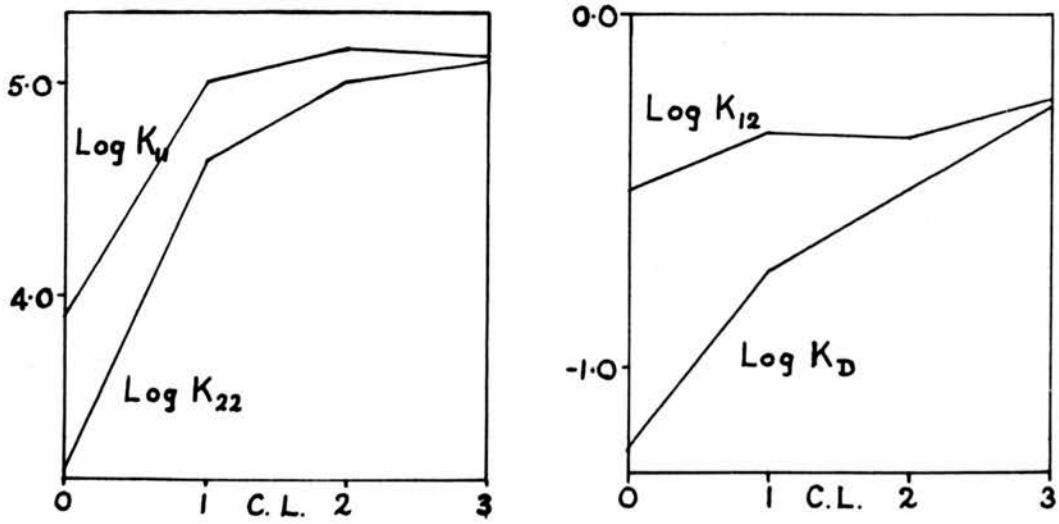


FIG. 4-13. Trend of the pairs of constants K_{11} and K_{22}, and K_{12} and K_D, towards common values with increase in chain length of normal acids. (C. L.)

(a) Log K_{11} and Log K_{22} (b) Log K_{12} and Log K_D



in each system the rest of the solution is largely composed of monomeric HA with small amounts (1-4%) of a and HA_2.

In mandelic acid the situation is quite different due to the formation of trimeric species, which are more stable than the dimeric species. At A = 400mM the maximum value of α_{12} (~7%) is comparable to the values in the other systems in which α_{12} is approximately 10-12% when A = 700mM. The value of α_{23} reaches a maximum of 13% at a pH of log K_{11}-0.1. However, the proportion of the dimer H_2A_2 is only 3% at the lowest pH reached, whereas α_{33} has a value of 28% at this point.

The values of pH at the points where two different α_{pq} curves intersect are related to the values of the stability constants. Thus, at the points where $\alpha_{01} = \alpha_{11}$ and $\alpha_{12} = \alpha_{22}$, pH = log K_{11} and log K_{22} respectively, and in the mandelate system pH = log K_{33} when $\alpha_{23} = \alpha_{33}$. This arises because, e.g. when a = [HA]

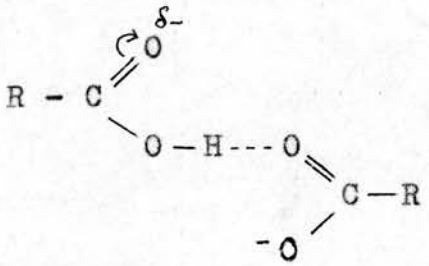
$$\bar{n}_1 = [HA]/(a + [HA]) = \tfrac{1}{2} \qquad (4\text{-}10)$$

and -log h = log K_{11} [cf. Sec 3 - C - a]. At the point where $\alpha_{01} = \alpha_{22}$, pH = log $K_{22}K_{12}$.

As would be expected the values of K_{11} determined in a 3.00M sodium (perchlorate) ionic medium at 25°C are greater than the so-called thermodynamic values by a roughly constant amount (0.2 to 0.3 log units). The values are also in the order expected from the inductive effects of the substituents, except for the propionic acid–butyric acid anomaly. Everett *et al*(1952) consider that it is propionic acid which is anomalous. They found that there are smooth

relationships between the chain length of carboxylic acids, and the free energy and entropy changes of ionisation, but propionic acid, not butyric acid deviates from these relationships. Dippy(1939) has suggested that the terminal methyl group of butyric acid may interact with the carbonyl group forming a hydrogen bond, so that the resulting stabilisation of the anion causes K_{11} to be less than expected. However, as ΔH is different for butyric and propionic acids, the order of K_{11} depends on the temperature. If the correct temperature is chosen this apparent anomaly disappears.

The evidence for the presence of polynuclear species in aqueous solution has been reviewed in Sec 1-C. In solution free rotation about the central hydrogen bond in the ions HA_2 is possible. However, the extended form,



which occurs as a structural unit in the crystal of salts of the type MHA_2, will be expected to predominate owing to the electrostatic repulsion between the partial negative charges on the two carboxyl groups.

The dimers H_2A_2 may adopt the open form, with only one hydrogen bond; the cyclic form, which occurs in the vapour state and perhaps in non polar solvents; or an equilibrium mixture of the two forms. The values in Table 4-9 show that $K_{22} \leq K_{11}$, i.e. the dimer is usually a stronger acid than the monomer. This supports the open form as the

structure of the dimer since a hydrogen bond would have to be broken as the cyclic form dissociates. Although, compared to other bonds, the energy of a hydrogen bond is small, it would probably be sufficient to make $K_{22} > K_{11}$. Moreover trimeric species can only be formed through the open form of the dimer. If the combinations of pairs of monomers to form dimers were chelations, then one might expect $K_D > K_{12}$. The trends found, $K_{11} \doteq K_{22} \gg K_{12} \doteq K_D$ are in the order expected for ion-ion, ion-dipole, and dipole-dipole interactions, and further suggest that the dimers exist predominantly in the extended form.

Support for the above argument has been obtained from a determination of the enthalpies and entropies of association for the acetate system. Enthalpy titrations were carried out by Schlyter and Martin(1961) using an adiabatic calorimeter at 25°C. Concentrations of the species present in the calorimeter were calculated and the enthalpies of association of HA, HA_2, and H_2A_2 computed from the heat data. The reality of the postulated equilibria (1-17), (1-18), and (1-19) and the values of the stability constants obtained potentiometrically are supported by the constancy of the values calculated for the enthalpies. Martin and Rossotti(1961) calculated the entropies of association ΔS and the values are given in Table 4-10 together with the values of the free energy ΔG and enthalpy changes ΔH.

The similarity of the values of ΔH and ΔS for the pair of reactions (a) and (b) suggests that the protonations are analogous, and that (b) is not a cyclisation. The same conclusion is reached for reactions (c) and (d) from the values of ΔH and ΔS for these reactions. As R

is almost the same in the phenylacetate, cyanoacetate, chloroacetate, and methoxyacetate systems as in the acetate system, it is likely that the neutral dimer has the open configuration in all these cases.

Table 4-10.

Thermodynamic Functions for Proton-Acetate Association in 3.00M Sodium Ionic Medium at 25°C.

Reaction	ΔG(kcal./mole)	ΔH(kcal./mole)	ΔS(e.u.)
a) $H + A \rightleftharpoons HA$	-6.839 ± 0.012	-0.721 ± 0.006	20.53 ± 0.06
b) $HA_2 + H \rightleftharpoons H_2A_2$	-6.315 ± 0.014	-0.596 ± 0.135	19.2 ± 0.5
c) $HA + A \rightleftharpoons HA_2$	0.46 ± 0.04	0.300 ± 0.106	-0.5 ± 0.5
d) $HA + HA \rightleftharpoons H_2A_2$	1.00 ± 0.04	0.425 ± 0.047	-1.9 ± 0.3

It is highly probable that the neutral dimer is a stronger acid than the monomer as a result of the formation of one hydrogen bond to give the open form. Apart from any movement of electrons associated with the inductive effect of the various substituents the hydrogen bond formed attracts electrons, thus causing the acidic hydrogen ion to be held less strongly in the dimer than in the monomer. Nevertheless, the values of the stability constants of the dimers H_2A_2 appear to be related to the inductive effects of the substituents, although the values of K_{22} and K_{11} are not in exactly the same order.

The inter-relationships $K_{22} = RK_{11}$ and $K_D = RK_{12}$ show that the differences between the pairs of constants K_{11} and K_{22}, and K_D and K_{12} are reflected by the position of the isohydric point. When

only the straight chain acids are considered, the trend in K_{12}, K_{22}, K_D, and R, as well as the trend in K_{11}, might be ascribed to the inductive effect. Figure 4-13 shows more clearly that the pairs of constants K_{11} and K_{22}, and K_{12} and K_D tend towards common values as the series formic to butyric acid is ascended. The equilibria present in the isobutyrate, valerate, and trimethylacetate systems were more complicated and this trend makes the assumption that R = 1 in these systems reasonable.

The hypothesis that the trends in the parameters might be ascribed to the inductive effect is not supported by the values of the stability constants for the substituted acetic acids. A similar value of R is found for the acetate, phenylacetate, cyanoacetate, chloroacetate, and methoxyacetate systems, and values of K_{12} and K_D are each equal, within experimental error, for acetate, cyanoacetate, and chloroacetate. To some extent, therefore, the trends in the stability constants appear to depend on the length of the carbon skeleton. It is possible that the apparent irregularity presented by the value of K_{12}, and consequently K_D, for phenylacetic acid is not real.

The parameters for glycollic and mandelic acids are unusual when compared with other substituted acetic acids. The values of R are so small as to suggest that the ions HA_2 are stabilised by intramolecular hydrogen bonding. However, this hypothesis may be incorrect, particularly as all the stability constants for the glycollate system are remarkably similar to those for the formate system. The exceptional stability of the trimer compared to the

dimer [log (K_{33}/K_{22})~0.5] is a further unusual feature in the mandelate system, and the trimer may conceivably be cyclic. This unexpected stability is also reflected in the high values of K_{DT} and K_T compared to K_D.

Finally, comparison of the stability constants for the propionate, isobutyrate and trimethylacetate systems, which have carbon backbones of the same length, suggests that chain-branching slightly enhances the formation of polynuclear species. However, the effect is no more than to bring isomeric systems (butyrate+isobutyrate; valerate trimethylacetate) roughly into line. A more complete and fundamental interpretation of the values of the various association constants must await the determination of the heats and entropies of association.

4 - C. APPENDIX OF RESULTS.

The potentiometric titration results for all the buffer titrations are summarised in this appendix. The following points should be noted:

a) All concentrations are in millimoles per litre.

b) The analyses were carried out with an experimental uncertainty of 0.1 to 0.2%. Concentrations are often quoted with more figures than justified by this precision for use in the calculations.

c) The analyses of buffers designated by numbers only will be found in the preceding table which refers to the same acid.

Table 4A-1.

Phenylacetic Acid.

Buffer	1		2		3	
[HA]	30.64		75.55		70.39	
A	700.6		1076		770.4	
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
20.02	6.254	0.038	20.73	5.759	0.058	20.32	5.590	0.091
49.77	6.009	0.042	50.38	5.728	0.066	49.70	5.590	0.091
69.60	5.983	0.042	68.31	5.728	0.067	69.09	5.596	0.091
100.1	5.973	0.043	100.2	5.733	0.068	99.19	5.605	0.091
149.8	5.978	0.043	150.4	5.745	0.070	149.8	5.625	0.091
199.3	5.992	0.043	200.5	5.765	0.070	199.6	5.645	0.091
300.0	6.030	0.044	299.9	5.811	0.070	300.0	5.692	0.091
399.4	6.087	0.044	399.6	5.860	0.070	400.1	5.742	0.091
500.5	6.151	0.044	500.2	5.909	0.070	499.9	5.799	0.091
601.0	6.202	0.044	599.9	5.962	0.070	600.5	5.855	0.091
700.6	6.254	0.044	710.0	6.021	0.070	700.4	5.909	0.091

Buffer	4		5		6	
[HA]	70.57		70.63		70.66	
A	350.8		200.7		140.7	
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
19.63	5.177	0.201	9.873	4.832	0.351	14.88	4.562	0.501
49.80	5.170	0.201	15.09	4.826	0.351	19.93	4.559	0.501
70.03	5.176	0.201	20.03	4.822	0.351	50.05	4.560	0.502
99.89	5.183	0.201	50.09	4.826	0.352	69.92	4.569	0.502
150.0	5.205	0.201	69.92	4.834	0.352	100.1	4.594	0.502
200.0	5.233	0.201	100.1	4.850	0.352	120.1	4.602	0.502
249.6	5.258	0.201	150.1	4.876	0.352	140.7	4.609	0.502
299.5	5.284	0.201	200.7	4.897	0.352			
350.8	5.304	0.201						

Buffer	7		8		9	
[HA]	70.67		70.68		71.62	
A	108.4		88.18		81.62	
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
9.940	4.297	0.647	10.06	3.958	0.792	4.935	3.751	0.864
14.96	4.288	0.649	15.03	3.958	0.795	9.936	3.730	0.869
20.02	4.286	0.650	20.06	3.958	0.797	20.10	3.722	0.872
50.03	4.285	0.651	49.94	3.969	0.799	49.91	3.720	0.874
69.98	4.295	0.651	70.14	3.975	0.800	70.01	3.729	0.875
99.82	4.312	0.652	88.18	3.979	0.800	81.62	3.735	0.875

Buffer	10		11		12	
[HA]	71.71		71.91		72.09	
A	79.63		75.42		73.94	
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
9.976	3.659	0.886	14.99	3.372	0.943	14.93	3.178	0.957
15.00	3.642	0.890	19.95	3.358	0.944	20.06	3.162	0.959
20.02	3.634	0.892	49.99	3.350	0.945	49.96	3.156	0.961
49.95	3.624	0.896	70.02	3.338	0.947	69.94	3.134	0.965
70.03	3.625	0.897	75.42	3.341	0.948	73.94	3.135	0.965
79.63	3.629	0.898						

Table 4A-2.

Cyanoacetic Acid A ≤ 100mM.

Buffer 1			2			3		
[HA]	59.91		95.96			146.9		
A	1486		1462			1464		
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
11.52	4.261	0.036	11.31	3.889	0.055	11.35	3.625	0.090
30.32	4.121	0.038	29.77	3.830	0.061	29.89	3.600	0.096
48.65	4.094	0.039	51.31	3.816	0.063	51.51	3.597	0.098
73.55	4.078	0.039	75.63	3.810	0.064	75.93	3.597	0.099
101.0	4.072	0.040	99.13	3.810	0.064	99.52	3.597	0.099

Buffer 4			5			6		
[HA]	294.6		517.8			744.5		
A	1471		1480			1490		
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
3.830	3.353	0.164	3.865	3.056	0.273	3.931	2.736	0.446
11.43	3.296	0.183	11.53	2.988	0.311	11.73	2.703	0.468
30.09	3.269	0.191	30.36	2.948	0.332	30.88	2.677	0.483
48.28	3.264	0.195	48.72	2.938	0.338	49.54	2.669	0.488
76.45	3.262	0.197	73.64	2.932	0.342	74.87	2.665	0.492
100.2	3.262	0.498	101.1	2.931	0.344	99.33	2.665	0.493

Buffer 7			8			9		
[HA]	975		1200			1350		
A	1500		1500			1500		
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
4.042	2.386	0.631	12.19	2.221	0.719	28.45	2.037	0.795
8.063	2.385	0.637	28.13	2.175	0.739	48.12	1.991	0.815
27.85	2.378	0.642	39.87	2.157	0.749	74.79	1.945	0.829
50.90	2.376	0.644	51.41	2.141	0.755	100.5	1.917	0.838
73.25	2.376	0.645	73.97	2.123	0.763			
98.47	2.376	0.646	99.42	2.109	0.769			

Buffer 10			11		
[HA]	1425		1500		
A	1500		1500		
A	pH	$\bar{n}$	A	pH	$\bar{n}$
28.61	1.979	0.817	28.61	1.947	0.831
48.38	1.922	0.839	48.38	1.871	0.853
75.18	1.866	0.855	75.18	1.800	0.872
97.38	1.834	0.865	97.38	1.759	0.884

Table 4A-3.

Cyanoacetic Acid A ≙ 100mM.

Buffer	1		2		3		4	
A	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$
100	4.072	0.040	3.810	0.064	3.597	0.099	3.262	0.198
200	4.072	0.040	3.816	0.065	3.603	0.100	3.271	0.199
300	4.084	0.040	3.828	0.065	3.615	0.100	3.281	0.199
400	4.094	0.040	3.840	0.065	3.629	0.100	3.292	0.200
500	4.106	0.040	3.854	0.065	3.641	0.100	3.303	0.200
600	4.119	0.040	3.865	0.065	3.654	0.100	3.313	0.200
700	4.131	0.040	3.877	0.065	3.666	0.100	3.325	0.200
800	4.143	0.040	3.889	0.066	3.678	0.100	3.335	0.200
900	4.155	0.040	3.903	0.066	3.691	0.100	3.347	0.200
1000	4.168	0.040	3.915	0.066	3.703	0.100	3.358	0.200

Buffer	5		6		7		8	
A	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$
100	2.931	0.344	2.665	0.493	2.376	0.646	2.109	0.769
200	2.936	0.347	2.667	0.496	2.378	0.647	2.086	0.781
300	2.943	0.348	2.672	0.497	2.383	0.647	2.077	0.786
400	2.951	0.348	2.679	0.497	2.388	0.647	2.072	0.787
500	2.959	0.348	2.686	0.498	2.393	0.647	2.070	0.790
600	2.970	0.349	2.694	0.498	2.398	0.647	2.070	0.791
700	2.978	0.349	2.701	0.498	2.402	0.647	2.070	0.792
800	2.988	0.349	2.708	0.498	2.408	0.647	2.070	0.792
900	2.998	0.349	2.718	0.498	2.414	0.647	2.072	0.793
1000	3.007	0.349	2.725	0.498	2.419	0.648	2.074	0.793

Buffer	9		10		11	
A	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$
100	1.917	0.838	1.831	0.866	1.754	0.885
200	1.856	0.858	1.738	0.888	1.629	0.911
300	1.825	0.867	1.688	0.900	1.551	0.924
400	1.805	0.872	1.651	0.907	1.494	0.932
500	1.786	0.876	1.634	0.912	1.450	0.938
600	1.775	0.879	1.604	0.915	1.409	0.942
700	1.768	0.880	1.587	0.918	1.377	0.945
800	1.759	0.882	1.570	0.920	1.347	0.947
900	1.753	0.883	1.557	0.922	1.322	0.950
1000	1.749	0.884	1.545	0.924	1.295	0.951

Table 4A-4,

Chloroacetic Acid A ≐ 100mM.

Buffer	1		2			3		
[HA]	73.11		144.8			300.7		
A	1501		1403			1501		
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
3.900	4.430	0.041	3.644	4.035	0.087	3.910	3.605	0.206
11.64	4.364	0.046	10.88	3.999	0.097	11.67	3.614	0.202
23.10	4.340	0.047	25.12	3.982	0.100	23.16	3.619	0.201
49.16	4.334	0.048	49.36	3.979	0.102	49.29	3.622	0.201
74.32	4.334	0.048	72.75	3.980	0.102	74.51	3.625	0.201
98.63	4.334	0.048	98.52	3.980	0.103	98.87	3.629	0.201

Buffer	4		5			6		
[HA]	528.3		877			979		
A	1502		1751			1506		
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
3.920	3.296	0.348	4.583	3.064	0.474	3.964	2.826	0.602
11.70	3.294	0.350	9.142	3.044	0.482	11.83	2.794	0.624
23.22	3.292	0.351	27.14	3.029	0.493	23.48	2.779	0.634
49.42	3.294	0.351	49.12	3.024	0.496	49.95	2.763	0.641
74.70	3.296	0.351	74.77	3.024	0.498	75.50	2.762	0.643
99.12	3.298	0.351	99.66	3.024	0.499	100.2	2.762	0.645

Buffer	7		8			9		
[HA]	1205		1356			1433		
A	1507		1508			1508		
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
4.041	2.473	0.781	4.131	2.238	0.853	24.72	2.089	0.890
8.060	2.466	0.783	8.239	2.228	0.857	48.65	2.048	0.901
23.93	2.452	0.788	24.45	2.202	0.868	75.60	2.015	0.907
50.90	2.444	0.792	48.12	2.175	0.873	101.6	1.989	0.911
73.25	2.442	0.793	74.80	2.158	0.878			
98.47	2.442	0.794	100.5	2.150	0.881			

Buffer	10	
[HA]	1754	
A	1754	
A	pH	$\bar{n}$
24.01	2.043	0.900
51.97	1.962	0.916
74.59	1.915	0.923
101.0	1.874	0.931

Table 4A-5.

Chloroacetic Acid A ≥ 100mM.

Buffer	1		2		3		4	
A	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$
100	4.334	0.048	3.980	0.103	3.629	0.201	3.298	0.351
200	4.351	0.049	3.994	0.103	3.641	0.200	3.309	0.352
300	4.361	0.049	4.007	0.103	3.651	0.200	3.320	0.352
400	4.373	0.049	4.019	0.103	3.666	0.200	3.330	0.352
500	4.386	0.049	4.033	0.103	3.680	0.200	3.340	0.352
600	4.400	0.049	4.046	0.103	3.690	0.200	3.348	0.352
700	4.415	0.049	4.060	0.103	3.703	0.200	3.360	0.352
800	4.427	0.049	4.072	0.103	3.715	0.200	3.370	0.352
900	4.440	0.049	4.084	0.103	3.727	0.200	3.382	0.352
1000	4.452	0.049	4.097	0.103	3.739	0.200	3.392	0.352

Buffer	5		6		7		8	
A	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$
100	3.024	0.499	2.762	0.645	2.442	0.794	2.150	0.881
200	3.030	0.500	2.763	0.647	2.442	0.796	2.126	0.886
300	3.039	0.500	2.767	0.648	2.446	0.796	2.118	0.889
400	3.047	0.500	2.774	0.648	2.449	0.797	2.114	0.890
500	3.054	0.500	2.780	0.648	2.451	0.797	2.111	0.891
600	3.063	0.501	2.785	0.648	2.456	0.797	2.109	0.892
700	3.069	0.501	2.794	0.649	2.459	0.797	2.109	0.892
800	3.079	0.501	2.799	0.649	2.463	0.797	2.108	0.893
900	3.088	0.501	2.806	0.649	2.466	0.797	2.108	0.893
1000	3.098	0.501	2.813	0.649	2.469	0.797	2.108	0.893

Buffer	9		10	
A	pH	$\bar{n}$	pH	$\bar{n}$
100	1.990	0.911	1.876	0.931
200	1.935	0.922	1.766	0.944
300	1.906	0.927	1.697	0.951
400	1.884	0.930	1.644	0.956
500	1.871	0.932	1.606	0.960
600	1.859	0.934	1.568	0.962
700	1.849	0.935	1.538	0.964
800	1.844	0.936	1.509	0.966
900	1.837	0.937	1.484	0.967
1000	1.830	0.938	1.460	0.968

Table 4A-6,

Glycollic Acid A ≤ 100mM.

Buffer	1		2			3		
[HA]	73.75		149.1			299.9		
A	1500		1500			1500		
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
26.79	5.297	0.049	3.896	4.880	0.098	3.896	4.526	0.199
49.00	5.253	0.049	11.63	4.871	0.099	11.63	4.520	0.200
101.7	5.231	0.049	26.85	4.870	0.099	26.85	4.520	0.200
			49.12	4.870	0.099	49.12	4.521	0.200
			98.54	4.876	0.099	98.54	4.526	0.200

Buffer	4		5			6		
[HA]	525.0		749.5			975		
A	1500		1500			1500		
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
3.896	4.188	0.350	3.906	3.852	0.531	3.906	3.615	0.673
11.63	4.188	0.350	11.66	3.898	0.511	11.66	3.637	0.658
26.85	4.190	0.350	26.92	3.913	0.505	26.92	3.647	0.653
49.12	4.192	0.350	49.24	3.916	0.502	49.24	3.647	0.652
98.54	4.193	0.350	98.78	3.921	0.501	98.78	3.647	0.651

Buffer	7		8			9		
[HA]	1199		1350			1420		
A	1500		1500			1500		
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
3.906	3.406	0.763	3.916	3.127	0.851	4.000	2.576	0.961
11.66	3.363	0.784	11.69	3.071	0.875	11.94	2.591	0.958
26.92	3.340	0.792	23.20	3.037	0.884	23.68	2.610	0.956
49.24	3.331	0.795	49.37	3.007	0.891	50.39	2.633	0.953
98.78	3.321	0.797	99.02	2.987	0.895	101.0	2.650	0.950

Table 4A-7.

Glycollic Acid A ≥ 100mM.

Buffer	1		2		3		4	
A	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$
100	5.231	0.049	4.876	0.099	4.526	0.200	4.193	0.350
200	5.231	0.049	4.885	0.099	4.533	0.200	4.200	0.350
300	5.240	0.049	4.898	0.099	4.543	0.200	4.207	0.350
400	5.250	0.049	4.908	0.099	4.550	0.200	4.210	0.350
500	5.258	0.049	4.919	0.099	4.560	0.200	4.215	0.350
600	5.272	0.049	4.930	0.099	4.567	0.200	4.222	0.350
700	5.279	0.049	4.939	0.099	4.575	0.200	4.226	0.350
800	5.290	0.049	4.949	0.099	4.584	0.200	4.231	0.350
900	5.301	0.049	4.957	0.099	4.592	0.200	4.237	0.350
1000	5.309	0.049	4.968	0.099	4.599	0.200	4.242	0.350

Buffer	5		6		7		8	
A	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$
100	3.921	0.501	3.647	0.651	3.321	0.797	2.987	0.895
200	3.926	0.500	3.647	0.650	3.316	0.798	2.970	0.897
300	3.928	0.500	3.647	0.650	3.309	0.798	2.959	0.898
400	3.930	0.500	3.647	0.650	3.303	0.799	2.948	0.898
500	3.931	0.500	3.647	0.650	3.298	0.799	2.939	0.898
600	3.933	0.500	3.646	0.650	3.292	0.799	2.931	0.899
700	3.935	0.500	3.646	0.650	3.287	0.799	2.922	0.899
800	3.938	0.500	3.646	0.650	3.282	0.799	2.914	0.899
900	3.942	0.500	3.644	0.650	3.277	0.799	2.907	0.899
1000	3.945	0.500	3.644	0.650	3.272	0.799	2.900	0.899

Buffer	9	
A	pH	$\bar{n}$
100	2.650	0.950
200	2.662	0.948
300	2.662	0.947
400	2.659	0.946
500	2.650	0.946
600	2.643	0.946
700	2.635	0.945
800	2.630	0.945
900	2.620	0.945
1000	2.613	0.945

Table 4A-8.

Methoxyacetic Acid A ≙ 100mM.

Buffer	1		2			3		
[HA]	99.53		201.8			306.0		
A	2003		2003			1505		
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
5.202	5.036	0.050	5.201	4.653	0.104	3.910	4.336	0.205
10.38	5.036	0.050	10.38	4.664	0.103	11.67	4.337	0.204
25.74	5.032	0.050	25.74	4.675	0.102	23.16	4.339	0.204
50.83	5.032	0.050	50.83	4.681	0.101	49.30	4.344	0.203
75.29	5.034	0.050	75.28	4.684	0.101	74.53	4.351	0.203
99.14	5.037	0.050	99.13	4.691	0.101	98.90	4.353	0.203

Buffer	4		5			6		
[HA]	702.4		1002			1303		
A	2002		2001			2001		
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
5.213	3.960	0.373	5. 211	3.720	0.512	5.210	3.484	0.641
10.40	3.979	0.362	10.40	3.729	0.506	10.39	3.478	0.646
25.79	3.994	0.356	25.79	3.735	0.503	25.78	3.473	0.649
50.93	3.999	0.353	50.92	3.739	0.502	50.90	3.473	0.650
75.44	4.001	0.353	75.42	3.742	0.502	75.40	3.473	0.651
99.34	4.008	0.352	99.31	3.744	0.501	99.28	3.473	0.651

Buffer	7		8			9		
[HA]	1604		1803			1905		
A	2000		2000			1999		
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
5.249	3.034	0.833	5.276	2.790	0.899	5.389	2.418	0.954
10.47	3.064	0.823	10.52	2.787	0.898	10.75	2.420	0.953
25.97	3.088	0.812	26.10	2.782	0.899	26.66	2.425	0.953
51.28	3.100	0.807	51.54	2.779	0.900	52.62	2.429	0.953
75.95	3.105	0.805	76.32	2.779	0.900	77.90	2.432	0.952
100.0	3.105	0.804	100.5	2.779	0.900	97.66	2.432	0.952

Buffer	10	
[HA]	1502	
A	1502	
A	pH	$\bar{n}$
8.250	2.202	0.970
24.48	2.178	0.973
48.18	2.146	0.974
74.88	2.119	0.976
100.6	2.096	0.977

Table 4A-9.

Methoxyacetic Acid A ≅ 100.

Buffer	1		2		3		4	
A	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$
100	5.037	0.050	4.691	0.101	4.353	0.203	4.008	0.352
200	5.054	0.050	4.708	0.101	4.368	0.203	4.021	0.351
300	5.071	0.050	4.724	0.101	4.384	0.203	4.035	0.351
400	5.088	0.050	4.740	0.101	4.400	0.203	4.048	0.351
500	5.105	0.050	4.757	0.101	4.413	0.203	4.062	0.351
600	5.122	0.050	4.774	0.101	4.427	0.203	4.074	0.351
700	5.139	0.050	4.789	0.101	4.440	0.203	4.085	0.351
800	5.156	0.050	4.804	0.101	4.454	0.203	4.099	0.351
900	5.172	0.050	4.819	0.101	4.471	0.203	4.112	0.351
1000	5.188	0.050	4.834	0.101	4.486	0.203	4.124	0.351

Buffer	5		6		7		8	
A	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$
100	3.744	0.501	3.473	0.651	3.105	0.804	2.779	0.900
200	3.754	0.501	3.478	0.651	3.113	0.803	2.779	0.900
300	3.766	0.501	3.485	0.651	3.118	0.802	2.779	0.901
400	3.774	0.501	3.492	0.651	3.123	0.802	2.780	0.901
500	3.786	0.501	3.499	0.651	3.127	0.802	2.782	0.901
600	3.795	0.501	3.507	0.651	3.132	0.802	2.782	0.901
700	3.806	0.501	3.512	0.651	3.135	0.802	2.782	0.901
800	3.817	0.501	3.521	0.651	3.137	0.802	2.784	0.901
900	3.827	0.501	3.528	0.651	3.140	0.802	2.787	0.901
1000	3.837	0.501	3.534	0.651	3.144	0.802	2.789	0.901

Buffer	9		10	
A	pH	$\bar{n}$	pH	$\bar{n}$
100	2.432	0.952	2.095	0.977
200	2.437	0.952	2.029	0.980
300	2.444	0.951	1.984	0.982
400	2.446	0.951	1.945	0.983
500	2.446	0.951	1.915	0.984
600	2.447	0.951	1.889	0.985
700	2.447	0.951	1.866	0.985
800	2.447	0.951	1.844	0.986
900	2.447	0.951	1.825	0.986
1000	2.447	0.951	1.806	0.986

Table 4A-10.

Potentiometric Titration of Phenoxyacetic Acid Solution.

Concentration of phenoxyacetic acid solution = 40.03mM.

Concentration of sodium hydroxide solution = 90.09mM.

E_o = 276.5mM.

V_B(ml.)	V_T(ml.)	C_B(mM)	C_{HA}(mM)	E(mV)	pH	C'_H(mM)	$\bar{n}$
—	18.00	—	—	227.3	2.168	6.789	—
—	24.00*	—	10.01	231.4	2.238	5.092	0.931
—	30.00*	—	16.01	233.9	2.280	4.073	0.927
—	36.00*	—	20.02	235.3	2.304	3.395	0.921
0.20	36.20	0.547	19.91	237.7	2.344	3.376	0.915
0.60	36.60	1.624	19.69	242.5	2.425	3.339	0.896
1.10	37.10	2.938	19.42	249.0	2.535	3.294	0.868
1.50	37.50	3.964	19.22	254.8	2.633	3.259	0.842
2.01	38.01	5.228	18.96	261.9	2.753	3.215	0.801
2.50	38.50	6.434	18.72	268.8	2.870	3.174	0.754
3.00	39.00	7.62	18.48	275.5	2.983	3.133	0.701
3.50	39.50	8.78	18.24	282.0	3.093	3.094	0.644
4.00	40.00	9.91	18.02	288.6	3.205	3.055	0.585
4.50	40.50	11.01	17.79	295.0	3.313	3.017	0.523
5.00	41.00	12.08	17.58	301.6	3.424	2.981	0.461
5.50	41.50	13.13	17.36	308.2	3.536	2.945	0.397
6.00	42.00	14.16	17.16	315.6	3.661	2.910	0.332
6.50	42.50	15.15	16.96	323.7	3.798	2.875	0.266
7.00	43.00	16.13	16.76	333.3	3.960	2.842	0.201
7.30	43.30	16.71	16.64	340.6	4.084	2.822	0.161
7.60	43.60	17.27	16.53	349.2	4.229	2.803	0.121
7.80	43.80	17.65	16.45	356.8	4.358	2.790	0.094
8.00	44.00	18.02	16.38	366.9	4.528	2.777	0.068
8.20	44.20	18.38	16.30	380.2	4.753	2.765	0.041
8.30	44.30	18.56	16.27	390.1	4.921	2.759	0.028

*Phenoxyacetic acid solution added.

Table 4A-11.

Mandelic Acid A ≤ 100mM.

Buffer	1		2		3	
$[HClO_4]$	69.69		139.4		278.7	
A	1400		1400		1400	
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
10.74	4.785	0.049	14.32	4.476	0.098	10.77	4.057	0.206
24.56	4.777	0.050	28.21	4.461	0.099	24.62	4.077	0.202
50.60	4.775	0.050	54.77	4.461	0.099	50.73	4.080	0.201
71.80	4.777	0.050	73.68	4.461	0.099	71.96	4.094	0.200
99.78	4.784	0.050	97.67	4.461	0.099	100.0	4.109	0.200

Buffer	4		5		6	
$[HClO_4]$	418.1		558		697	
A	1400		1400		1400	
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
10.77	3.844	0.299	24.69	3.636	0.402	7.235	3.482	0.503
24.62	3.850	0.299	50.85	3.651	0.400	24.69	3.473	0.499
50.73	3.861	0.299	72.13	3.656	0.399	50.85	3.482	0.498
71.96	3.872	0.299	100.2	3.673	0.399	72.13	3.489	0.498
100.0	3.877	0.299				100.2	3.499	0.498

Buffer	7		8		9	
$[HClO_4]$	836		976		1115	
A	1400		1400		1400	
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
24.69	3.316	0.593	24.75	3.123	0.691	24.87	2.900	0.792
50.85	3.320	0.595	50.97	3.127	0.694	51.22	2.894	0.793
72.13	3.321	0.596	72.30	3.130	0.695	72.64	2.894	0.794
100.0	3.330	0.596	100.4	3.132	0.695	100.9	2.909	0.794

Buffer	10		11		12	
$[HClO_4]$	1252		1324		1394	
A	1400		1400		1400	
A	pH	$\bar{n}$	A	pH	$\bar{n}$	A	pH	$\bar{n}$
48.76	2.547	0.890	50.26	2.244	0.947	50.26	2.128	0.961
73.68	2.559	0.891	71.43	2.222	0.943	75.86	2.096	0.962
99.54	2.567	0.892	97.03	2.233	0.943	99.53	2.072	0.964

Table 4A-12.

Mandelic Acid A ≅ 100mM.

Buffer	1		2		3		4	
A	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$
100	4.784	0.050	4.461	0.099	4.109	0.200	3.877	0.299
150	4.799	0.050	4.481	0.099	4.126	0.200	3.893	0.299
200	4.814	0.050	4.498	0.099	4.143	0.199	3.908	0.299
250	4.831	0.050	4.515	0.099	4.160	0.199	3.923	0.299
300	4.850	0.050	4.532	0.100	4.177	0.199	3.940	0.299
350	4.868	0.050	4.549	0.100	4.194	0.199	3.957	0.299
400	4.887	0.050	4.566	0.100	4.211	0.199	3.972	0.299
450	4.907	0.050	4.582	0.100	4.277	0.199	3.989	0.299
500	4.927	0.050	4.601	0.100	4.244	0.199	4.006	0.299

Buffer	5		6		7		8	
A	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$
100	3.673	0.399	3.499	0.498	3.330	0.596	3.132	0.695
150	3.688	0.399	3.514	0.498	3.340	0.596	3.144	0.695
200	3.703	0.398	3.526	0.498	3.348	0.597	3.156	0.696
250	3.717	0.398	3.539	0.498	3.358	0.597	3.162	0.696
300	3.732	0.398	3.551	0.498	3.370	0.597	3.174	0.696
350	3.746	0.398	3.566	0.498	3.380	0.597	3.183	0.696
400	3.759	0.398	3.580	0.498	3.391	0.597	3.193	0.696
450	3.773	0.398			3.402	0.597	3.201	0.696

Buffer	9		10		11		12	
A	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$	pH	$\bar{n}$
100	2.909	0.794	2.567	0.892	2.240	0.944	2.072	0.964
150	2.912	0.795	2.584	0.892	2.248	0.943	2.047	0.968
200	2.912	0.795	2.582	0.892	2.275	0.944	2.013	0.969
250	2.919	0.795	2.584	0.891	2.290	0.944	1.979	0.970
300	2.929	0.795	2.593	0.891	2.292	0.943	1.964	0.971
350	2.936	0.795	2.601	0.891	2.298	0.943	1.950	0.972
400	2.944	0.795	2.606	0.891	2.314	0.943	1.933	0.973
450	2.951	0.795	2.616	0.891	2.315	0.942	1.923	0.974
500			2.623	0.891	2.319	0.942	1.923	0.975

Table 4A-13.

Potentiometric Titration of Mandelic Acid Solution.

Concentration of stock mandelic acid solution = 100.7mM.

Constant concentration during titration = 20.14mM.

Concentration of sodium hydroxide solution = 99.13mM.

E_o = 277.0mV.

V_{HA}(ml.)	V_B(ml.)	V_T(ml.)	C_B(mM)	E(mV)	pH	C'_H(mM)	$\bar{n}$
0.00	0.00	18.00	—	227.5	2.163	6.869	—
4.50	0.00	22.50	—	229.0	2.189	5.495	0.951
4.60	0.40	23.00	1.724	236.0	2.307	5.376	0.936
4.70	0.80	23.50	3.375	244.0	2.442	5.261	0.914
4.80	1.20	24.00	4.956	253.0	2.594	5.152	0.883
4.90	1.60	24.50	6.473	262.1	2.748	5.047	0.841
5.00	2.00	25.00	7.93	271.1	2.900	4.946	0.789
5.10	2.40	25.50	9.33	279.5	3.042	4.849	0.733
5.20	2.80	26.00	10.68	287.0	3.169	4.756	0.673
5.30	3.20	26.50	11.97	294.0	3.287	4.666	0.612
5.40	3.60	27.00	13.22	300.4	3.396	4.579	0.551
5.50	4.00	27.50	14.42	306.5	3.499	4.496	0.492
5.60	4.40	28.00	15.58	312.5	3.600	4.416	0.433
5.70	4.80	28.50	16.69	318.8	3.707	4.338	0.377
5.80	5.20	29.00	17.77	325.0	3.812	4.264	0.322
5.90	5.60	29.50	18.82	331.7	3.925	4.191	0.268
6.00	6.00	30.00	19.83	339.0	4.048	4.121	0.216
6.10	6.40	30.50	20.80	347.6	4.194	4.054	0.165
6.20	6.80	31.00	21.74	358.1	4.371	3.989	0.116
6.25	7.00	31.25	22.20	365.0	4.488	3.957	0.092
6.30	7.20	31.50	22.66	373.4	4.630	3.925	0.069
6.35	7.40	31.75	23.10	384.6	4.819	3.894	0.046

C H A P T E R. 5

COPPER CARBOXYLATE EQUILIBRIA.

The equilibria which occur in the copper(II) phenylacetate, cyanoacetate, chloroacetate, glycollate, methoxyacetate, mandelate, and phenoxyacetate systems have been carefully studied to determine whether dinuclear complexes are formed in aqueous solution. As the carboxylate ligands are the conjugate bases of weak acids the experimental approach has been to follow the competitive complex formation between protons and copper(II) ions for the ligands.

At least two different buffer solutions with a difference in pH of not less than 0.4 units, and several copper concentrations ranging from 10mM to 100mM, were used in each system. Berecki-Biedermann(1956) has shown that polynuclear hydrolysis of the copper(II) ion occurs between pH4 and 5, depending on the concentration of copper. Accordingly, buffer solutions of pH's appropiate to avoid hydrolysis were used. Different buffers and copper concentrations were used to show whether mixed complexes of the type BHA_2, or polynuclear complexes $B_qA_p(q \geq 2)$ respectively, were formed. In no instance did the copper(II) ion concentration represent more than 3.3%, and the free carboxylate ion more than 18% of the ionic medium, and the activity coefficients of all species appear to remain constant under these conditions (Biedermann and Sillén 1953).

5 - A. RESULTS.

Details of the experimental procedure have been given in Sec 2-D-c, and of the calculation of $\bar{n}$ and a in Sec 3-G-a. Complete data for a

typical copper(II) - carboxylate titration are given in Table 5-1. The term C_H' arises from the dilution of the perchloric acid remaining when the E_o titration is stopped. In titrations where the copper(II) concentration is held constant there is an additional term, h_{Cu}, which arises from the acid in the copper(II) perchlorate solution. The total hydrogen ion concentration, H, therefore is given by

$$H = [HA] + C_H' + h_{Cu} \qquad (5\text{-}1)$$

The experimental data for the copper(II) carboxylate titrations are plotted in the form $\bar{n}(\log a)$, and the shape of such curves gives some insight into the complexes present. Formation curves, $\bar{n}(\log a)_B$, may be functions of the different metal ion concentrations used in the titrations thereby indicating polynuclear formation. This dependence would also be apparent in titrations where B is allowed to vary over different ranges of concentrations. Further titrations in which B is held constant would then be required to simplify the interpretation. Variation of the formation curves with buffer ratio would show that mixed complexes were being formed.

If the formation curve rises to a plateau at an integral value, N, of $\bar{n}$, and does not subsequently rise again, then the highest complex formed, within the limits of the experimental measurements, is BA_N. On the other hand the formation curve may form an intermediate plateau at, say, $\bar{n} = 1$, and then rise again to form a second plateau at $\bar{n} = 2$. This indicates that the first complex is much stronger than the second. In many instances, however, it is impossible to reach any plateau, and the number of complexes present is not immediately apparent from an inspection of the formation curve. Nevertheless,

Experimental data for a copper (II) chloroacetate titration

Buffer composition : HA = 528.3 mM; A = 1502 mM E_o = 265.0 mV

V_{Bu}	V_T	HA	A	E(mV)	pH	h	C'_H	$\bar{n}_H$	B	$\bar{n}$	- log a
0.00	20.00	-	-	214.6	2.148	-	7.09	-	100.0	-	-
0.05	20.05	1.318	3.744	220.1	2.241	5.741	7.07	0.855	99.8	0.007	3.348
0.15	20.15	3.933	11.18	231.3	2.430	3.712	7.04	0.794	99.3	0.021	2.725
0.25	20.25	6.522	18.54	238.8	2.557	2.773	7.00	0.743	98.8	0.041	2.430
0.40	20.40	10.36	29.44	245.8	2.676	2.111	6.95	0.686	98.0	0.074	2.158
0.60	20.60	15.39	43.73	251.1	2.765	1.718	6.88	0.641	97.1	0.120	1.939
1.00	21.00	25.16	71.50	256.6	2.858	1.387	6.75	0.591	95.2	0.209	1.680
1.70	21.70	41.39	117.6	261.4	2.939	1.150	6.533	0.547	92.2	0.349	1.418
2.80	22.80	64.88	184.4	265.8	3.014	0.969	6.217	0.506	87.7	0.522	1.175
5.00	25.00	105.7	300.3	270.7	3.096	0.801	5.670	0.464	80.0	0.776	0.913
7.70	27.70	146.9	417.4	274.4	3.159	0.694	5.118	0.434	72.2	0.953	0.728
12.00	32.00	198.1	563.1	278.0	3.220	0.603	4.430	0.410	62.5	1.129	0.569
18.00	38.00	250.3	711	281.1	3.272	0.534	3.370	0.391_5	52.6	1.214	0.441
25.00	45.00	293.5	834	283.1	3.306	0.494	3.150	0.381	44.44	1.279	0.359

The volumes are given in ml., and V_{Bu} = volume of buffer added. Concentrations are given in millimoles per litre, except [~~-log~~] a which is in moles per litre.

even in those cases, it is possible to reach a reasonable conclusion as to the number of complexes present. Two examples will illustrate this. The formation curve for copper(II) cyanoacetate, Fig. 5-1, has only one point above $\bar{n} = 1$, but as there is no tendency to form a plateau, there must be at least two complexes present in solution. Likewise the formation curve for copper(II) glycollate, Fig. 5-3, goes beyond $\bar{n} = 2$ indicating that the highest complex is at least BA_3.

The experimental data for the copper(II) cyanoacetate, chloroacetate, glycollate, methoxyacetate, phenoxyacetate, mandelate, and phenylacetate titrations are given in Tables 5-2 to 5-8 inclusive and the respective formation curves in Figs. 5-1 to 5-7. The heading for each titration gives the composition of the buffer used in terms of carboxylic acid and total carboxylate concentration; the approximate pH of the buffer solution for $A \leq 50mM$; the concentration of copper(II) used, and whether it was allowed to vary; and the symbol used for that particular titration in the appropiate figure. When the copper(II) concentration was allowed to vary the difference between the first and any subsequent value of V_T gives the volume of buffer added. Half this difference gives the volume of buffer added when the copper(II) concentration was held constant. The concentration range of free carboxylate ion for any system may be seen more readily from the $\bar{n}$(log a) curves than by scrutinising the tabulated experimental data.

(Text continued on p.116.)

FIG. 5-1 Formation curve for copper(II) cyanoacetate

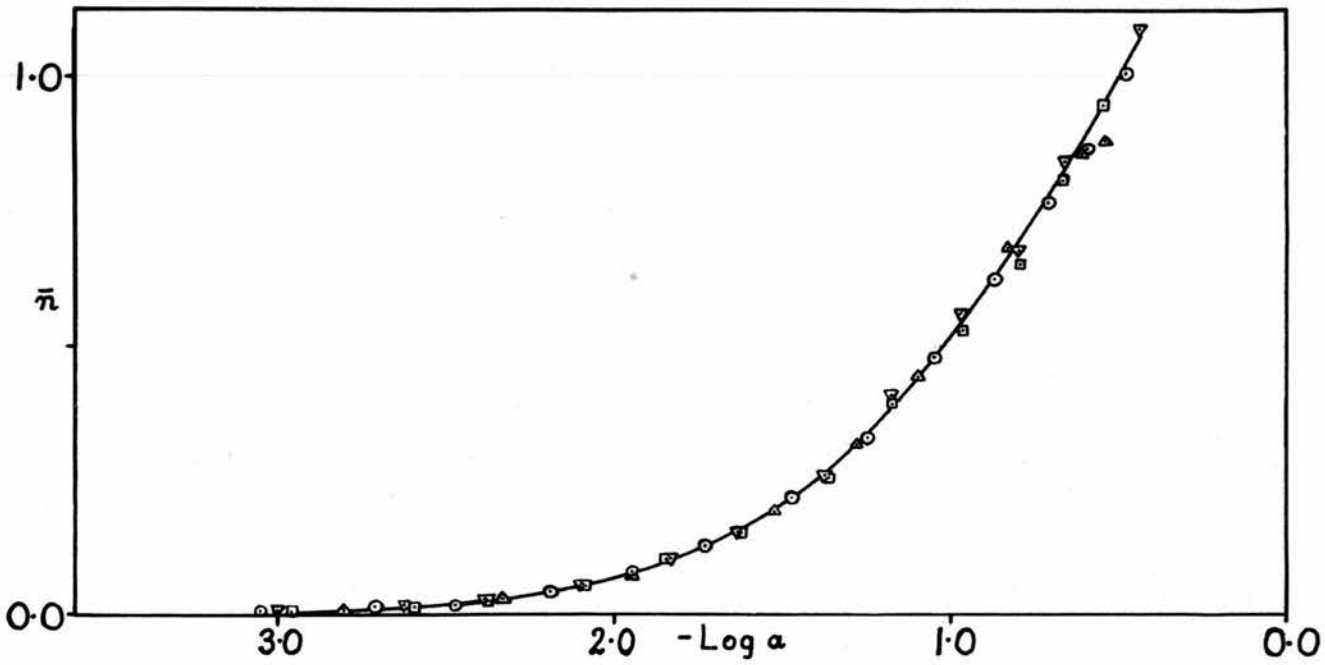


FIG. 5-2 Formation curve for copper(II) chloroacetate

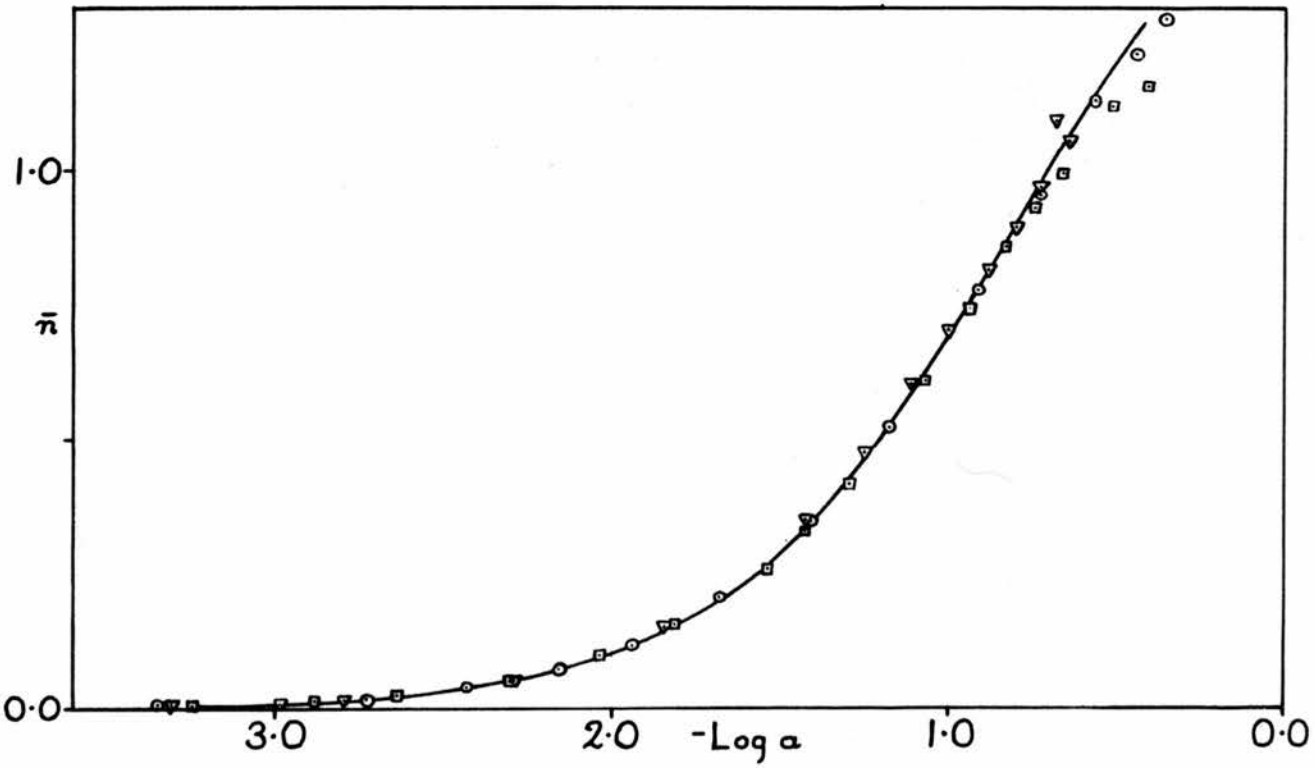


Table 5-2.

Copper(II) Cyanoacetate.

Buffer: [HA] = 251.1mM
A =150.1mM pH 3.33
B = 50.0mM at V_T = 20.00ml.
and allowed to vary.
Symbol. ⊡

V_T(ml.)	pH	$\bar{n}$	-log a
20.00	2.175	—	∞
20.05	2.307	0.006	2.955
20.10	2.425	0.015	2.592
20.15	2.527	0.028	2.369
20.25	2.672	0.056	2.086
20.40	2.802	0.104	1.841
20.60	2.916	0.153	1.620
21.00	3.024	0.256	1.365
21.60	3.107	0.392	1.173
22.50	3.172	0.529	0.965
23.70	3.223	0.653	0.793
25.30	3.267	0.808	0.655
27.10	3.298	0.948	0.547

Buffer: [HA] = 251.1mM
A =150.1mM pH 3.33
B = 100.0mM. at V_T = 20.00ml.
and allowed to vary.
Symbol. ⊙

V_T(ml.)	pH	$\bar{n}$	-log a
20.00	2.148	—	∞
20.05	2.253	0.007	3.047
20.10	2.344	0.017	2.708
20.15	2.439	0.020	2.473
20.25	2.574	0.047	2.190
20.40	2.701	0.083	1.943
20.60	2.806	0.129	1.729
21.00	2.917	0.219	1.472
21.60	3.010	0.334	1.246
22.50	3.086	0.479	1.051
23.70	3.147	0.625	0.869
25.30	3.200	0.768	0.712
27.10	3.242	0.866	0.594
30.00	3.287	1.007	0.477

Buffer: [HA] = 251.1mM
A =150.1mM pH 3.33
B = 50.0mM at V_T = 20.00ml.
and allowed to vary.
Symbol. ▽

V_T(ml.)	pH	$\bar{n}$	-log a
20.00	2.175	—	∞
20.05	2.292	0.011	3.000
20.10	2.407	0.023	2.626
20.15	2.523	0.029	2.373
20.25	2.667	0.060	2.094
20.40	2.801	0.106	1.831
20.60	2.910	0.158	1.625
21.00	3.020	0.260	1.369
21.60	3.101	0.408	1.178
22.50	3.167	0.564	0.970
23.70	3.220	0.677	0.797
25.30	3.260	0.844	0.662
30.00	3.328	1.090	0.436

Buffer: [HA] = 499.2mM
A =150.1mM pH 2.94
B = 95.2$_4$mM at V_T = 21.00ml.
and allowed to vary
Symbol. △

V_T(ml.)	pH	$\bar{n}$	-log a
21.00	2.037	—	∞
21.10	2.158	0.010	2.801
21.15	2.211	0.018	2.623
21.25	2.305	0.031	2.327
21.50	2.446	0.075	1.943
22.20	2.601	0.194	1.519
23.00	2.677	0.318	1.278
24.00	2.731	0.443	1.096
26.60	2.807	0.686	0.830
31.00	2.880	0.859	0.609
33.00	2.902	0.881	0.540

Table 5-3.

Copper(II) Chloroacetate.

Buffer: [HA] = 979mM
A =1506mM pH 2.75
B = 50.0mM at V_T = 20.00ml.,
and allowed to vary.
Symbol. ▽

V_T(ml.)	pH	$\bar{n}$	-log a
20.00	2.175	—	∞
20.05	2.221	0.003	3.302
20.10	2.255	0.010	2.986
20.15	2.285	0.017	2.789
20.40	2.393	0.055	2.287
21.00	2.493	0.151	1.843
22.50	2.572	0.351	1.423
23.70	2.605	0.475	1.251
25.30	2.635	0.602	1.112
27.10	2.660	0.704	1.000
30.00	2.691	0.814	0.883
33.20	2.714	0.892	0.801
37.00	2.733	0.969	0.732
41.00	2.748	1.091	0.683
45.00	2.760	1.052	0.643

Buffer: [HA] = 528mM
A =1501mM pH 3.29
B = 50.0mM at V_T = 20.00ml.,
and allowed to vary.
Symbol. ⊡

V_T(ml.)	pH	$\bar{n}$	-log a
20.00	2.176	—	∞
20.05	2.300	0.004	3.243
20.10	2.410	0.016	2.880
20.15	2.512	0.028	2.632
20.25	2.672	0.052	2.301
20.40	2.799	0.100	2.035
20.60	2.894	0.158	1.811
21.00	2.990	0.261	1.538
21.30	3.029	0.332	1.425
21.70	3.064	0.416	1.293
22.80	3.127	0.611	1.069
23.80	3.161	0.742	0.935
25.00	3.189	0.860	0.830
26.30	3.215	0.931	0.746
27.70	3.237	0.993	0.662
32.00	3.279	1.117	0.516
38.00	3.314	1.155	0.407

Buffer: [HA] = 528mM
A =1502mM pH 3.29
B = 100.0mM at V_T = 20.00ml.,
and allowed to vary.
Symbol. ⊙

V_T(ml.)	pH	$\bar{n}$	-log a
20.00	2.149	—	∞
20.05	2.241	0.007	3.348
20.15	2.430	0.021	2.725
20.25	2.557	0.041	2.430
20.40	2.676	0.074	2.158
20.60	2.765	0.120	1.939
21.00	2.858	0.209	1.680
21.70	2.939	0.349	1.418
22.80	3.014	0.522	1.175
25.00	3.096	0.776	0.913
27.70	3.159	0.953	0.728
32.00	3.220	1.129	0.569
38.00	3.272	1.214	0.441
45.00	3.306	1.279	0.359

FIG. 5-3 Formation curve for copper(II) glycollate

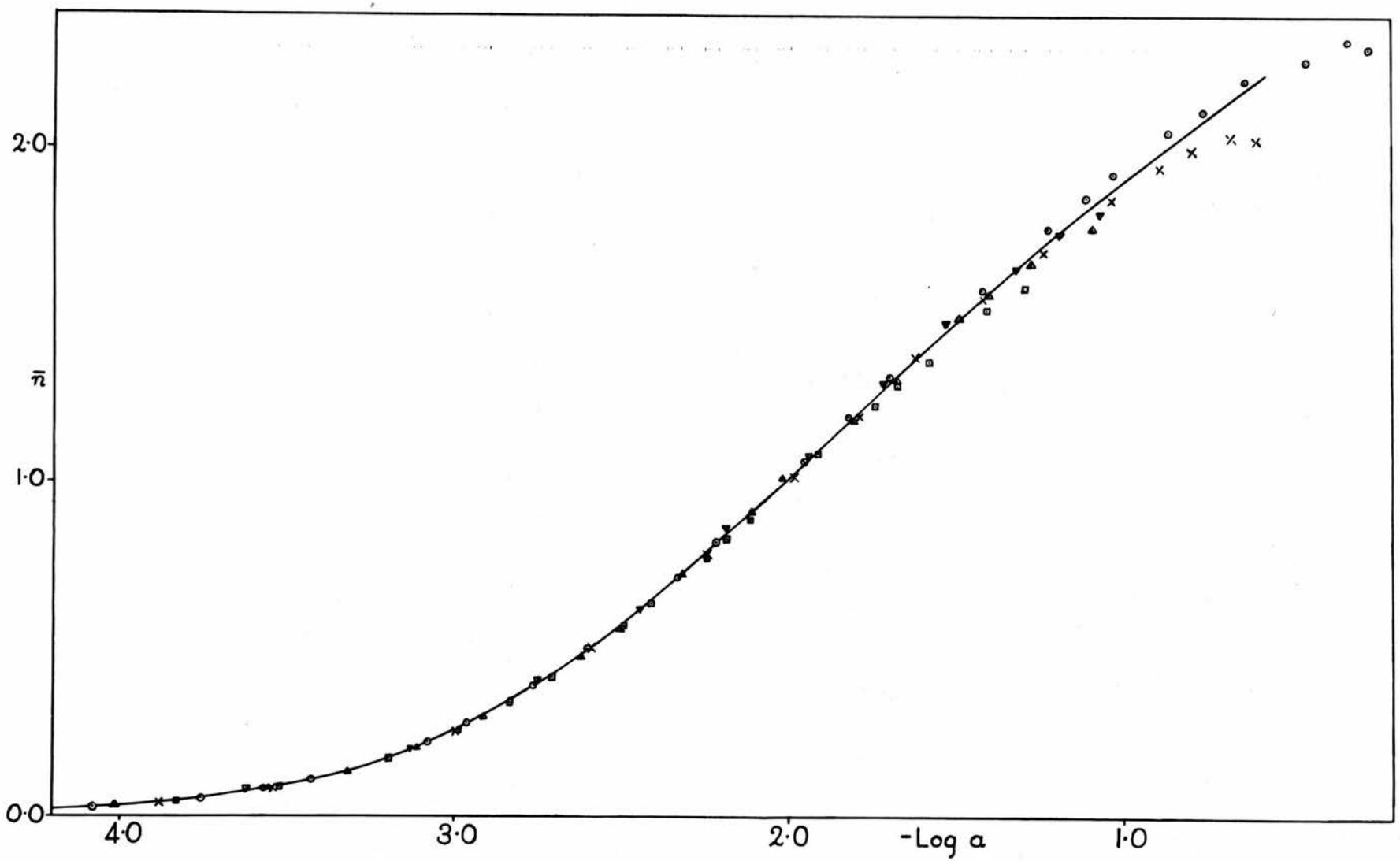


Table 5-4.

Copper(II) Glycollate.

Buffer: [HA] = 299.9mM
A =1500mM pH 4.52
B = 100.0mM at V_T = 20.00ml.,
and allowed to vary.
Symbol. ⊙

V_T(ml.)	pH	$\bar{n}$	-log a
20.00	2.748	—	∞
20.05	2.828	0.026	4.079
20.10	2.877	0.054	3.761
20.15	2.909	0.082	3.573
20.20	2.941	0.110	3.429
20.40	3.015	0.224	3.080
20.50	3.049	0.280	2.961
20.70	3.113	0.392	2.765
20.90	3.174	0.503	2.605
21.30	3.296	0.718	2.335
21.50	3.355	0.822	2.222
22.00	3.502	1.065	1.959
22.30	3.588	1.197	1.824
22.60	3.668	1.317	1.701
23.40	3.852	1.576	1.424
24.20	3.984	1.760	1.230
24.70	4.045	1.855	1.115
25.20	4.099	1.923	1.036
26.50	4.198	2.050	0.869
27.50	4.253	2.112	0.766
29.50	4.327	2.205	0.640
34.00	4.415	2.264	0.457
40.00	4.471	2.327	0.334
45.00	4.501	2.305	0.271

Buffer: [HA] = 975mM
A =1500mM pH 3.65
B = 25.00mM at V_T = 20.00ml.,
and allowed to vary.
Symbol. ⊡

V_T(ml.)	pH	$\bar{n}$	-log a
20.00	2.665	—	∞
20.05	2.684	0.043	3.843
20.10	2.703	0.086	3.527
20.20	2.735	0.172	3.197
20.30	2.767	0.256	2.987
20.40	2.799	0.339	2.837
20.50	2.836	0.416	2.709
20.70	2.900	0.569	2.498
20.80	2.934	0.638	2.415
21.00	2.997	0.774	2.250
21.10	3.025	0.830	2.189
21.20	3.054	0.886	2.118
21.60	3.154	1.086	1.914
22.00	3.230	1.229	1.745
22.20	3.262	1.287	1.681
22.50	3.303	1.359	1.582
23.30	3.379	1.512	1.409
24.00	3.426	1.580	1.297

Table 5-4 contd.

Buffer: [HA] = 975mM
A = 1500mM pH 3.65
B = 50.0mM at V_T = 20.00ml,
and allowed to vary.
Symbol. △

V_T(ml.)	pH	$\bar{n}$	-log a
20.00	2.628	—	∞
20.05	2.577	0.030	4.018
20.15	2.545	0.083	3.554
20.25	2.542	0.133	3.320
20.40	2.547	0.205	3.111
20.60	2.571	0.298	2.911
21.00	2.637	0.476	2.623
21.20	2.677	0.561	2.509
21.60	2.755	0.726	2.323
22.10	2.851	0.912	2.115
22.40	2.909	1.013	2.021
23.00	3.014	1.182	1.808
23.51	3.085	1.305	1.682
24.50	3.198	1.490	1.493
25.00	3.238	1.560	1.407
26.00	3.306	1.655	1.278
28.00	3.396	1.759	1.100

Buffer: [HA] = 975mM
A = 1500mM pH 3.65
B = 25.00mM (constant)
h_{Cu} = 0.412mM Symbol.

V_T(ml.)	pH	$\bar{n}$	-log a
18.40	2.451	—	∞
18.60	2.540	0.080	3.626
18.90	2.640	0.202	3.131
19.40	2.753	0.407	2.753
20.00	2.860	0.624	2.450
20.80	2.978	0.867	2.194
21.80	3.093	1.082	1.947
23.22	3.200	1.298	1.722
25.00	3.281	1.476	1.535
28.40	3.367	1.640	1.324
32.40	3.418	1.744	1.194
38.40	3.458	1.806	1.075

Buffer: [HA] = 525mM
A = 1500mM pH 4.19
B = 50.0mM (constant)
h_{Cu} = 0.824mM
Symbol. ×

V_T(ml.)	pH	$\bar{n}$	-log a
19.00	2.657	—	∞
19.10	2.773	0.038	3.883
19.20	2.841	0.081	3.544
19.60	2.970	0.257	2.994
20.20	3.100	0.502	2.594
21.00	3.250	0.786	2.248
21.80	3.382	1.016	1.987
22.60	3.485	1.199	1.791
23.60	3.588	1.374	1.626
25.00	3.691	1.547	1.420
27.00	3.789	1.687	1.239
31.00	3.891	1.845	1.037
36.00	3.950	1.942	0.896
43.00	3.996	1.996	0.797
55.00	4.029	2.036	0.684
69.00	4.051	2.025	0.606

FIG. 5-4 Formation curve for copper(II) methoxyacetate

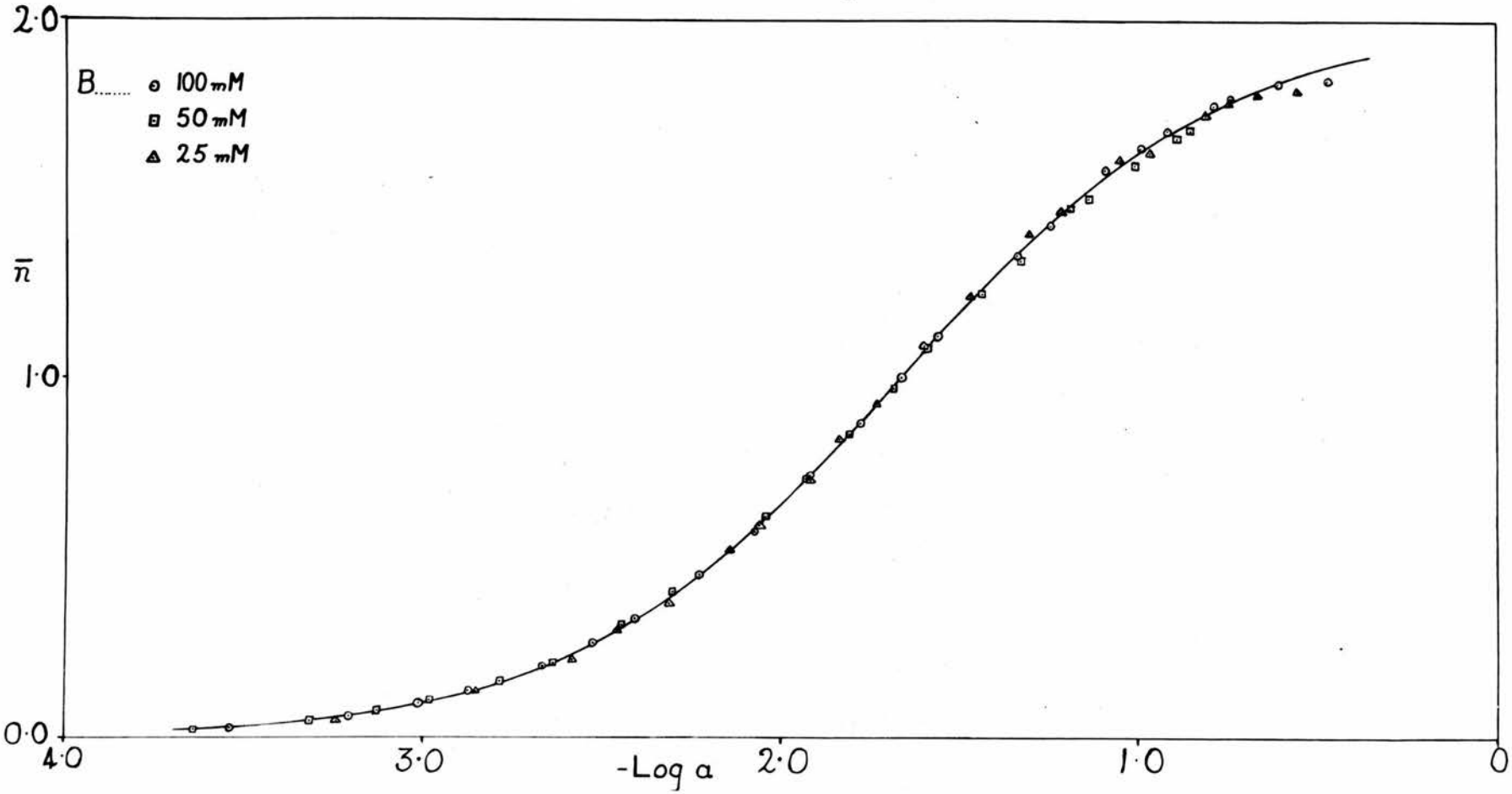


Table 5-5.

Copper(II) Methoxyacetate.

Buffer: [HA] = 399mM.
A = 2002mM. pH 4.34
B = 100.0mM. (constant)
h_{Cu} = 1.648mM. Symbol. ⊙

V_T(ml.)	pH	$\bar{n}$	-log a
19.60	2.613	—	∞
19.70	2.866	0.027	3.542
19.80	2.987	0.061	3.211
19.90	3.058	0.096	3.013
20.00	3.108	0.131	2.872
20.20	3.178	0.199	2.667
20.40	3.223	0.267	2.525
20.60	3.264	0.333	2.406
21.00	3.321	0.457	2.230
21.40	3.375	0.573	2.073
22.00	3.446	0.733	1.923
22.60	3.507	0.879	1.779
23.20	3.566	1.005	1.664
23.81	3.619	1.120	1.562
25.40	3.737	1.344	1.340
26.20	3.784	1.429	1.249
28.20	3.877	1.585	1.093
29.60	3.930	1.643	0.993
31.00	3.972	1.694	0.920
34.60	4.045	1.762	0.790
36.60	4.075	1.783	0.744
43.60	4.143	1.824	0.611
60.60	4.216	1.834	0.473

Buffer: [HA] = 702mM.
A = 2002mM. pH 4.00
B = 25.00mM. (constant)
h_{Cu} = 0.4119mM. Symbol. △

V_T(ml.)	pH	$\bar{n}$	-log a
19.20	2.544	—	∞
19.30	2.937	0.044	3.247
19.40	3.122	0.129	2.852
19.51	3.250	0.219	2.585
19.60	3.298	0.299	2.458
19.704	3.362	0.376	2.313
19.90	3.429	0.522	2.144
20.00	3.458	0.592	2.060
20.20	3.509	0.719	1.918
20.40	3.550	0.834	1.838
20.60	3.585	0.935	1.733
21.00	3.644	1.093	1.600
21.40	3.686	1.233	1.472
22.20	3.751	1.403	1.308
22.80	3.786	1.470	1.215
24.20	3.840	1.614	1.052
25.20	3.871	1.632	0.970
28.20	3.916	1.737	0.812
30.20	3.937	1.771	0.744
33.20	3.959	1.795	0.670
41.20	3.992	1.804	0.555

Buffer: [HA] = 1303mM.
A = 2001mM. pH 3.46
B = 50.0mM. (constant)
h_{Cu} = 0.8238mM. Symbol. ⊡

V_T(ml.)	pH	$\bar{n}$	-log a
19.00	2.435	—	∞
19.10	2.496	0.023	3.647
19.20	2.537	0.049	3.319
19.30	2.566	0.076	3.130
19.40	2.589	0.102	2.984
19.60	2.623	0.157	2.785
19.80	2.652	0.209	2.637
20.20	2.692	0.313	2.444
20.60	2.728	0.407	2.305
21.60	2.799	0.617	2.042

contd.

V_T(ml.)	pH	$\bar{n}$	-log a
22.20	2.838	0.724	1.929
23.00	2.880	0.848	1.808
24.00	2.929	0.976	1.687
25.00	2.968	1.083	1.591
27.00	3.036	1.237	1.439
29.00	3.088	1.327	1.329
33.00	3.149	1.474	1.192
35.00	3.174	1.502	1.138
43.00	3.233	1.598	1.011
61.00	3.291	1.671	0.893
69.00	3.303	1.694	0.854

FIG. 5-5 Formation curve for copper(II) phenoxyacetate

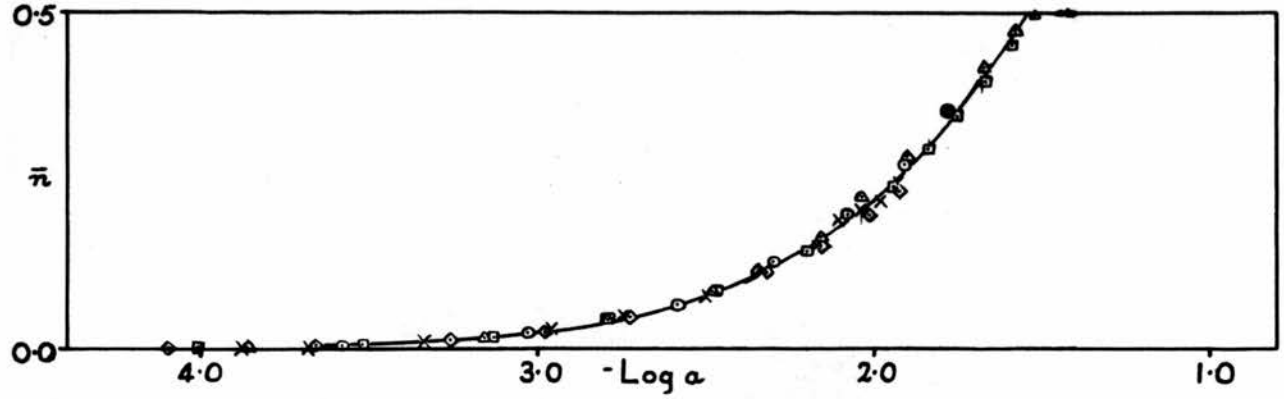


FIG. 5-6 Formation curve for copper(II) mandelate

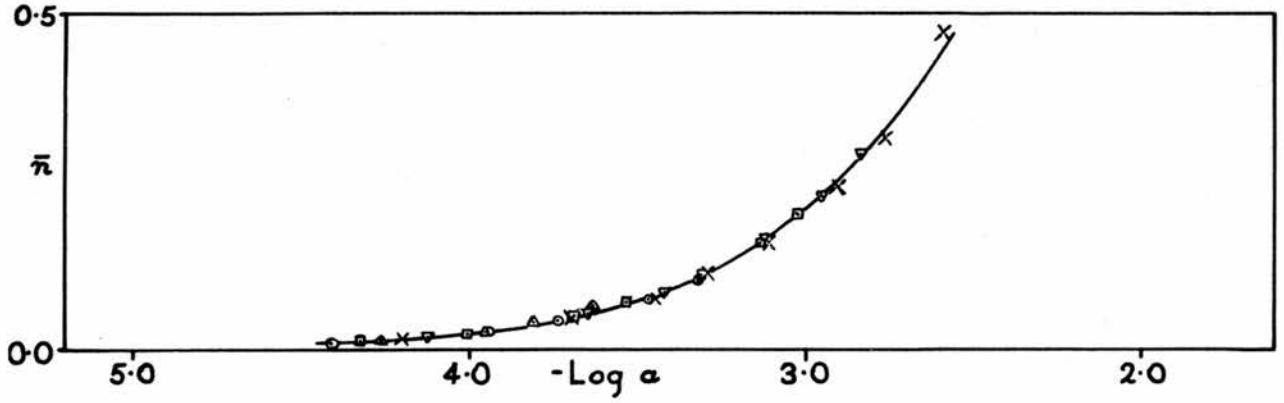


FIG. 5-7 Formation curve for copper(II) phenylacetate

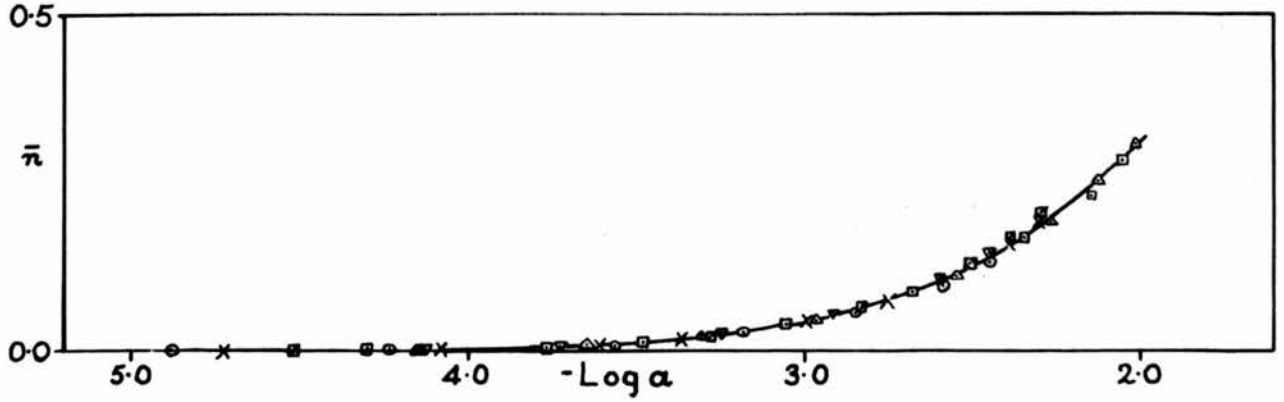


Table 5-6.

Copper(II) Phenoxyacetate

Buffer: [HA] = 20.00mM

A = 100.0mM pH 3.96

B = 25.00mM at V_T = 17.00ml., and allowed to vary. Symbol △

V_T(ml.)	pH	$\bar{n}$	-log a
18.40	2.894	—	∞
18.50	2.980	0.003	3.860
18.80	3.189	0.018	3.155
19.20	3.360	0.042	2.789
19.90	3.504	0.086	2.478
20.40	3.561	0.117	2.344
21.40	3.637	0.169	2.156
22.40	3.678	0.226	2.038
23.90	2.724	0.289	1.904
25.90	3.766	0.354	1.779
28.40	3.800	0.421	1.674
31.40	3.827	0.476	1.584
34.40	3.850	0.499	1.516

Buffer: [HA] = 20.00mM

A = 100.0mM pH 3.96

B = 100.0mM at V_T = 19.00ml., and allowed to vary. Symbol ⊡

V_T(ml.)	pH	$\bar{n}$	-log a
18.90	3.019	—	∞
19.00	3.063	0.002	4.009
19.20	3.129	0.008	3.526
19.60	3.213	0.019	3.113
20.40	3.301	0.042	2.788
21.90	3.386	0.083	2.473
24.40	3.467	0.146	2.201
28.90	3.553	0.243	1.945
31.90	3.592	0.298	1.838
34.90	3.629	0.345	1.754
43.90	3.705	0.454	1.590

Buffer: [HA] = 29.25mM

A = 60.0 mM pH 3.36

B = 10.00mM (constant)

h_{Cu} = 0.850mM Symbol ×

V_T(ml.)	pH	$\bar{n}$	-log a
18.80	2.476	—	∞
19.44	2.542	0.000	3.881
19.80	2.576	0.003	3.679
20.80	2.662	0.013	3.338
22.80	2.812	0.031	2.958
24.80	2.916	0.050	2.745
29.00	3.046	0.079	2.495
34.80	3.122	0.116	2.331
40.80*	3.183	0.154	2.188
43.80*	3.210	0.191	2.107
46.80*	3.233	0.208	2.038
49.80*	3.252	0.221	1.984
53.80*	3.269	0.247	1.931

* After adding 10ml. of both buffer and copper solutions, addition of copper was discontinued. Hence 12ml. of buffer solution were added at V_T = 40.80ml. and so on.

Buffer: [HA] = 20.00mM

A = 100.0mM pH 3.96

B = 25.00mM (constant)

h_{Cu} = 2.125mM Symbol ⊙

V_T(ml.)	pH	$\bar{n}$	-log a
19.80	2.872	—	∞
20.20	3.019	0.006	3.575
21.00	3.216	0.025	3.031
22.80	3.423	0.069	2.583
25.80	3.541	0.130	2.296
30.80	3.617	0.199	2.080
39.80	3.666	0.276	1.913
58.00	3.700	0.356	1.783

Buffer: [HA] = 29.25mM

A = 60.0 mM pH 3.36

B = 50.0mM at V_T = 18ml.,

and allowed to vary. Symbol ◇

V_T(ml.)	pH	$\bar{n}$	-log a
18.00	2.383	—	∞
18.30	2.420	0.003	4.089
18.70	2.473	0.007	3.657
19.50	2.572	0.014	3.258
20.50	2.672	0.027	2.980
22.00	2.785	0.048	2.724
24.10	2.888	0.076	2.504
27.00	2.978	0.113	2.321
31.00	3.056	0.153	2.160
37.00	3.130	0.198	2.014
43.00	3.174	0.235	1.925

Table 5-6.

Copper(II) Mandelate

Buffer: [HA] = 130.8mM
A = 200.5mM pH 3.21
B = 50.0mM(constant)
h_{Cu} = 4.25mM Symbol ⊙

V_T(ml.)	pH	$\bar{n}$	-log a
19.00	2.368	-	∞
19.20	2.356	0.009	4.408
19.60	2.339	0.026	3.942
20.00	2.325	0.042	3.737
21.00	2.305	0.077	3.462
22.00	2.288	0.108	3.313

Buffer: [HA] = 68.6mM
A = 200.5mM pH 3.77
B = 50.0mM(constant)
h_{Cu} = 4.25mM Symbol △

V_T(ml.)	pH	$\bar{n}$	-log a
20.20	2.877	-	∞
20.40	2.845	0.014	4.260
20660	2.824	0.027	3.951
20.80	2.801	0.040	3.808
21.20	2.760	0.065	3.632

Buffer: [HA] = 130.8mM
A = 200.5mM pH 3.21
B = 10.00mM(constant)
h_{Cu} = 0.850mM Symbol ×

V_T(ml.)	pH	$\bar{n}$	-log a
18.40	2.346	-	∞
18.60	2.364	0.016	4.198
19.00	2.403	0.047	3.694
19.40	2.442	0.075	3.441
19.80	2.469	0.112	3.290
20.40	2.511	0.160	3.105
21.40	2.564	0.244	2.908
22.40	2.610	0.317	2.764
24.40	2.655	0.473	2.593

Buffer: [HA] = 27.42mM
A = 80.2mM pH 3.77
B = 10.00mM(constant)
h_{Cu} = 0.850mM Symbol ▽

V_T(ml.)	pH	$\bar{n}$	-log a
19.80	3.189	-	∞
20.00	3.198	0.018	4.122
20.40	3.210	0.053	3.647
20.80	3.223	0.085	3.419
21.80	3.242	0.162	3.128
22.80	3.260	0.229	2.956
23.80	3.276	0.290	2.835

Buffer: [HA] = 130.8mM
A = 200.5mM pH 3.21
B = 25.00mM(constant)
h_{Cu} = 2.125mM Symbol ⊡

V_T(ml.)	pH	$\bar{n}$	-log a
18.60	2.332	-	∞
18.80	2.339	0.013	4.332
19.00	2.342	0.024	4.006
19.42	2.354	0.048	3.690
19.80	2.359	0.070	3.532
20.60	2.376	0.112	3.310
21.60	2.396	0.159	3.132
22.60	2.407	0.208	3.024

Table 5-8.

Copper(II) Phenylacetate

Buffer: [HA] = 70.7mM, A = 140.7mM used for 4 titrations below. pH 4.56

B = 10.00mM (constant)

h_{Cu} = 0.1878mM Symbol △

V_T (ml.)	pH	$\bar{n}$	-log a
23.00	3.380		
23.20	3.693	0.002	4.149
23.40	3.945	0.010	3.641
23.70	4.114	0.021	3.303
24.00	4.192	0.034	3.106
24.30	4.241	0.045	2.965
24.60	4.271	0.056	2.863
25.40	4.317	0.085	2.673
26.20	4.342	0.110	2.546
27.40	4.364	0.144	2.413
29.40	4.386	0.190	2.266
32.60	4.403	0.251	2.124
36.70	4.415	0.308	2.012

B = 10.00mM (constant)

h_{Cu} = 0.1878mM Symbol □

V_T (ml.)	pH	$\bar{n}$	-log a
23.00	3.264		
23.20	3.527	0.001	4.293
23.40	3.793	0.005	3.766
23.60	3.960	0.013	3.476
23.90	4.092	0.026	3.214
24.20	4.165	0.039	3.050
24.60	4.220	0.055	2.896
25.50	4.288	0.088	2.676
26.60	4.327	0.123	2.512
28.40	4.361	0.168	2.341
30.00	4.378	0.201	2.240
32.00	4.393	0.229	2.145
35.00	4.405	0.282	2.053

B = 40.0mM (constant)

h_{Cu} = 0.751mM Symbol ⊙

V_T (ml.)	pH	$\bar{n}$	-log a
23.00	3.167	—	
23.10	3.250	0.001	4.879
23.30	3.440	0.002	4.231
23.60	3.659	0.007	3.760
24.20	3.857	0.019	3.337
24.60	3.921	0.027	3.180
25.00	3.962	0.035	3.063
26.20	4.026	0.057	2.843
27.40	4.062	0.077	2.698
28.70	4.084	0.097	2.594
32.40	4.109	0.132	2.447

B = 25.00mM (constant)

h_{Cu} = 0.470mM Symbol ×

V_T (ml.)	pH	$\bar{n}$	-log a
23.00	3.267		
23.10	3.387	0.000	4.721
23.30	3.609	0.003	4.076
23.60	3.837	0.010	3.605
23.90	3.953	0.019	3.360
24.30	4.035	0.030	3.153
24.80	4.090	0.043	2.988
26.00	4.153	0.073	2.749
27.80	4.193	0.112	2.549
30.40	4.217	0.159	2.383
32.40	4.229	0.190	2.300

Table 5-8 contd.

Buffer: [HA] = 71.3mM
A = 251.4mM pH 4.97
B = 40.0mM(constant)
h_{Cu} = 0.751mM Symbol ▼

V_T(ml.)	pH	$\bar{n}$	-log a
23.20	3.531	-	∞
23.30	3.913	0.004	4.128
23.40	4.114	0.009	3.722
23.50	4.209	0.015	3.509
23.70	4.310	0.027	3.246
23.90	4.359	0.039	3.082
24.20	4.406	0.056	2.911
24.60	4.440	0.078	2.755
25.20	4.469	0.109	2.596
25.60	4.484	0.128	2.515
26.00	4.493	0.147	2.449

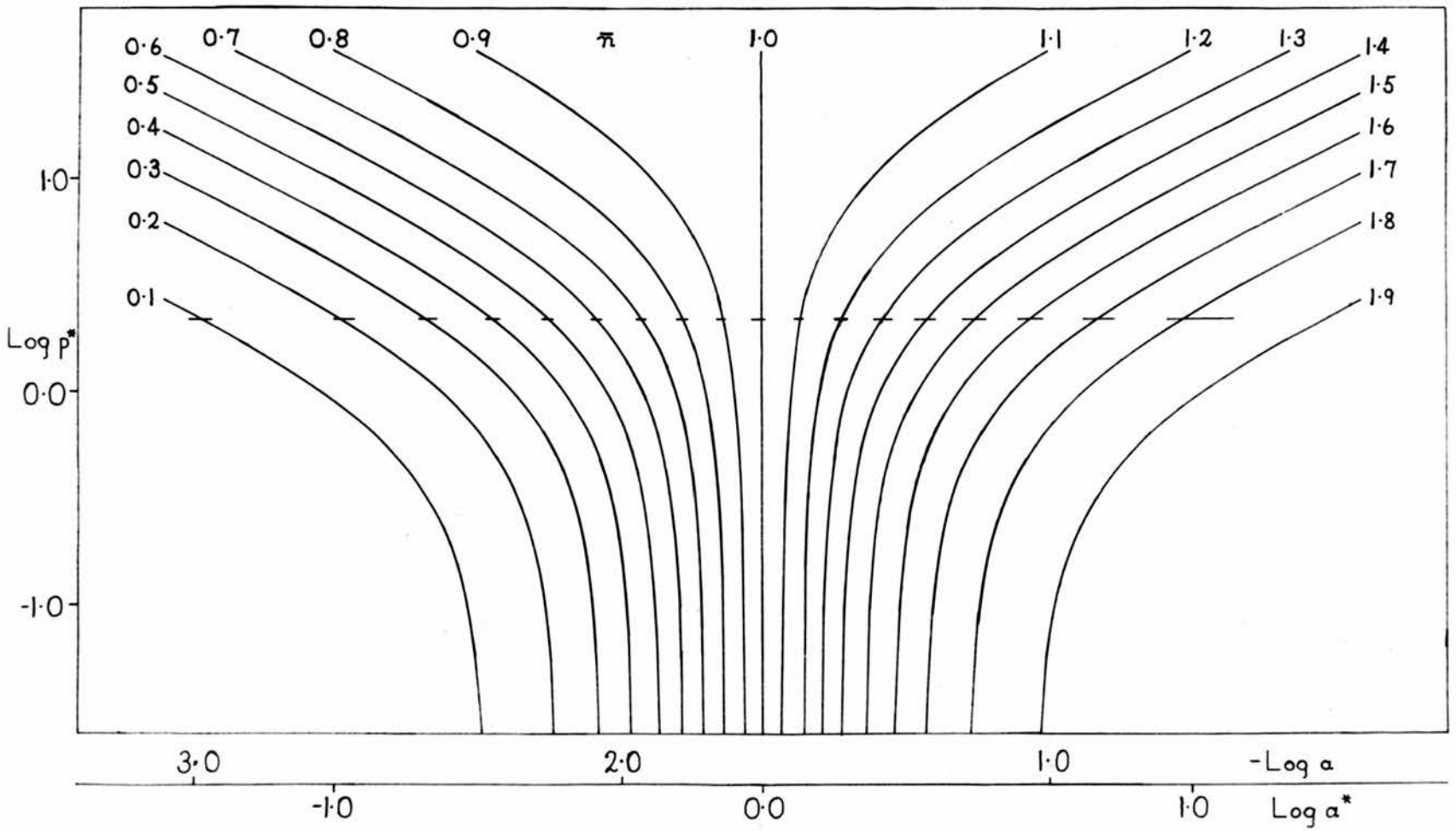
Buffer: [HA] = 70.6mM
A = 200.7mM pH4.82
B = 20.00mM(constant)
h_{Cu} = 0.376mM Symbol ◪

V_T(ml.)	pH	$\bar{n}$	-log a
23.00	3.284	-	∞
23.10	3.494	0.003	4.516
23.30	3.988	0.010	3.629
23.50	4.200	0.020	3.276
23.70	4.273	0.034	3.104
24.20	4.379	0.064	2.829
24.60	4.423	0.087	2.691
25.40	4.469	0.136	2.508
26.20	4.493	0.168	2.383
26.60	4.503	0.187	2.334
27.00	4.508	0.205	2.293

Figures 5-1 to 5-7 show clearly that all the formation curves are independent of the metal ion concentrations and salt:acid ratios of the buffers used. This implies that only homonuclear complexes are detectable and that mixed complexes of any kind do not occur. Since the lowest copper(II) concentration was 10mM, the complexes were assumed to be mononuclear.

The extent of the measurements in the phenoxyacetate, mandelate, and phenylacetate systems was restricted to $\bar{n} \leq 0.5$ by the precipitation of the copper(II) carboxylate. Whilst no precipitation occurred in the other systems, copper(II) glycollate crystals appeared when the titrated solutions were allowed to stand overnight, and copper(II) cyanoacetate crystals were obtained from the solution after a few days. In the cyanoacetate and chloroacetate systems the complexes are considerably less stable than in other systems. The possible error associated with high free carboxylate concentration determined the maximum value

FIG. 5-8 Normalised $\log p^*(\log a^*)_{\pi}$ curves calculated using Eq.(3-89) with the projection strip for copper(II) methoxyacetate in the position of best fit.



of $\bar{n}$ reached. A maximum possible error of $\pm$ 0.4mV in $E - E_o$ in these titrations gives rise to a variation of the order of $\pm$ 0.1 in $\bar{n}$ for the highest values of $\bar{n}$.

Only in the glycollate and methoxyacetate systems do the formation curves reach values of $\bar{n}$ much in excess of $\bar{n} = 1$. The formation curve for the former rises to $\bar{n} = 2.3$ without forming a plateau at any stage. This indicates that the complexes formed must be BA, BA_2, BA_3 at least. On the other hand the formation curve for copper(II) methoxyacetate tends towards a plateau at $\bar{n} = 2$, and is symmetrical about the mid point, where $\bar{n} = 1$. Thus only two complexes were detected in this system within the limits of the experimental measurements.

The stability constants for the complexes BA and BA_2 in all the systems were obtained by the projection strip method which has been fully described in Sec.3 - G - c. The family of log $p^*(\log a^*)_{\bar{n}}$ curves are shown in Fig. 5-8 with the projection strip for copper(II) methoxyacetate in the position of best fit. Equations (3-93) and (3-94) give

$$\log K_1 = \log p^* - \log a_o \qquad (5\text{-}2)$$

and

$$\log K_2 = -\log p^* - \log a_o \qquad (5\text{-}3)$$

and Eq.(3-92) gives

$$\log \beta_2 = -2\log a_o \qquad (5\text{-}4)$$

Table 5-9 gives the values of log p^* and log a_o at the positions of best fit, and the corresponding values of log K_1, log K_2, and log β_2 for the copper(II) carboxylates studied excluding the glycollate system. As the data only extend to $\bar{n} = 0.3$ in the phenylacetate system the projection strip fitted the log $p^*(\log a^*)_{\bar{n}}$

Table 5-9.

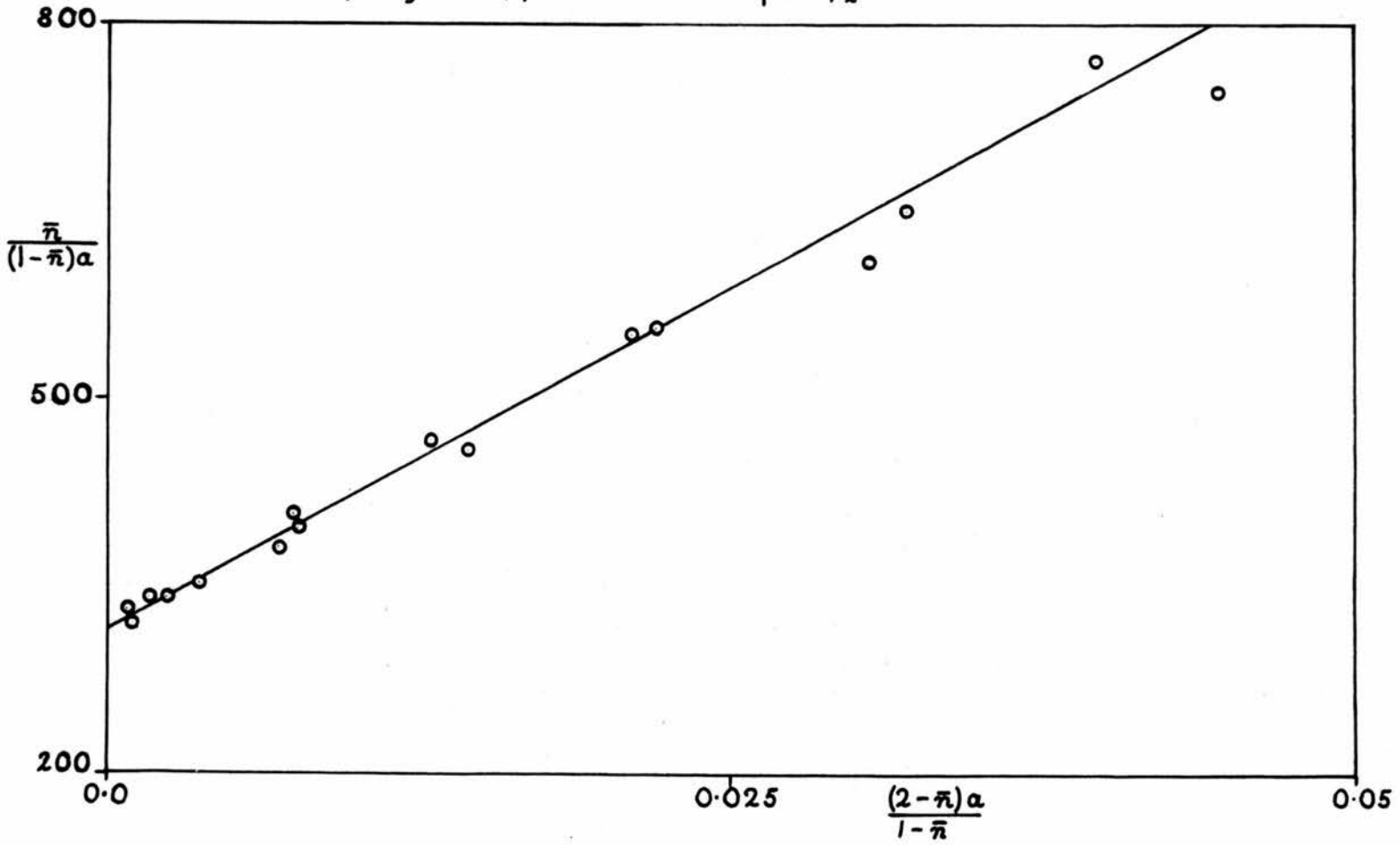
Stability Constants for Copper(II) Carboxylates by Projection Strip Method.

Copper(II) cyanoacetate	Copper(II) chloroacetate
$\log p^* = 0.37 \pm 0.02_5$	$\log p^* = 0.31 \pm 0.02_5$
$-\log a_o = 0.50 \pm 0.01_5$	$-\log a_o = 0.71_5 \pm 0.01_5$
$\log K_1 = 0.87 \pm 0.02$	$\log K_1 = 1.02_5 \pm 0.02$
$\log K_2 = 0.13 \pm 0.02$	$\log K_2 = 0.40_5 \pm 0.02$
$\log \beta_2 = 1.00 \pm 0.03$	$\log \beta_2 = 1.43 \pm 0.03$
Copper(II) methoxyacetate	**Copper(II) phenoxyacetate**
$\log p^* = 0.34 \pm 0.02_5$	$\log p^* = 0.42 \pm 0.03$
$-\log a_o = 1.67 \pm 0.01_5$	$-\log a_o = 0.99 \pm 0.01_5$
$\log K_1 = 2.01 \pm 0.02$	$\log K_1 = 1.41 \pm 0.02_5$
$\log K_2 = 1.33 \pm 0.02$	$\log K_2 = 0.57 \pm 0.02_5$
$\log \beta_2 = 3.34 \pm 0.03$	$\log \beta_2 = 1.98 \pm 0.03$
Copper(II) mandelate	**Copper(II) phenylacetate**
$\log p^* = 0.40 \pm 0.02_5$	$\log p^* \geq 0.42$
$-\log a_o = 1.98 \pm 0.01_5$	$-\log a_o = 1.19$
$\log K_1 = 2.38 \pm 0.02$	$\log K_1 = 1.61 \pm 0.02_5$
$\log K_2 = 1.58 \pm 0.02$	$\log K_2 \leq 0.8$
$\log \beta_2 = 3.96 \pm 0.03$	$\log \beta_2 \leq 2.4$

curves at all values of log p* above log p* = 0.42. A maximum value was therefore obtained for log K_2. The variation quoted for log K_1 was obtained by fitting the results on the mononuclear curve [Sec.3 - G - b] from which the same value was found for log K_1. The full lines in Figs. 5-1, 5-2, and 5-4 to 5-7 are the

FIG. 5-9 Copper(II) glycollate

Evaluation of β_1 and β_2 by the method of successive extrapolation
The intercept gives β_1 and the slope β_2.



the theoretical curves for the constants quoted. These curves were obtained from the positions of best fit on the projection strip.

Since at least three complexes were present in the glycollate system the projection strip method could not be used to obtain accurate values of β_1 and β_2. Approximate values of β_1 and β_2 were obtained, however,by fitting the projection strip to the family of $\log p^*(\log a^*)_{\bar{n}}$ curves. A fit was possible up to $\bar{n} = 1.5$ and in the position of best fit $\log p^* = 0.48 \pm 0.02_5$ and $-\log a_o = 2.02 \pm 0.02_5$ Whence, using Eqs. (5-2) and (5-4)

$$\log \beta_1 = 2.50 \pm 0.02 \qquad \log \beta_2 = 4.04 \pm 0.03$$

These values were refined, and the value of β_3 computed, by the method of successive extrapolations detailed in Sec.3 - H. The first extrapolation is shown in Fig. 5-9 where the plot of $\bar{n}/(1 - \bar{n})a$ against $(2 - \bar{n})a/(1 - \bar{n})$ gives β_1 as intercept and β_2 as slope. The values obtained for the stability constants are

$$\log \beta_1 = 2.50 \pm 0.02$$

$$\log \beta_2 = 4.02 \pm 0.04 \qquad \log K_2 = 1.52 \pm 0.02$$

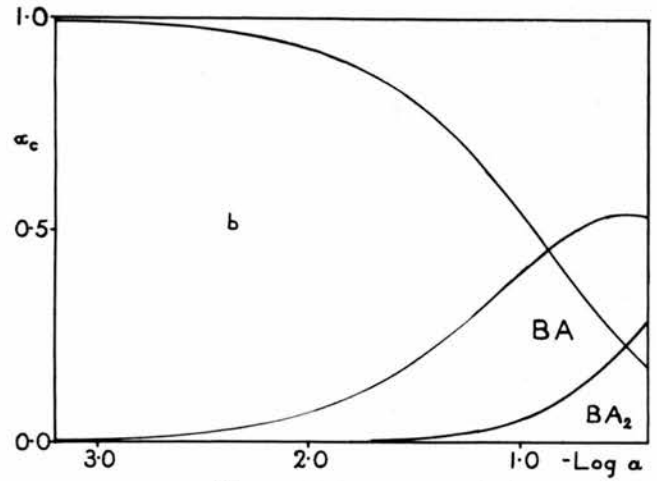
$$\log \beta_3 = 4.27 \pm 0.10 \qquad \log K_3 = 0.25 \pm 0.06$$

After determining these constants a theoretical formation curve was calculated from them using Eq. (1-8) in the particular form

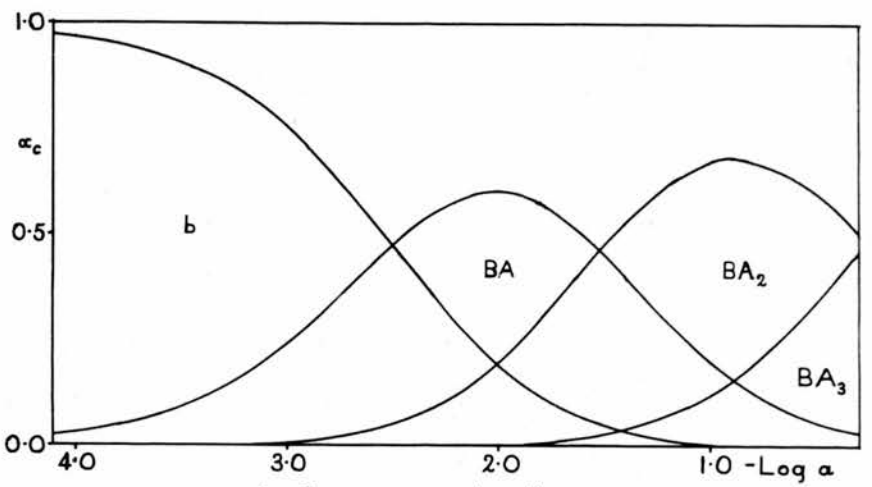
$$\bar{n} = \frac{\beta_1 a + 2\beta_2 a^2 + 3\beta_3 a^3}{1 + \beta_1 a + \beta_2 a^2 + \beta_3 a^3} \qquad (5\text{-}5)$$

The curve obtained is the full line in Fig. 5-3, and it fits the experimental data with high precision.

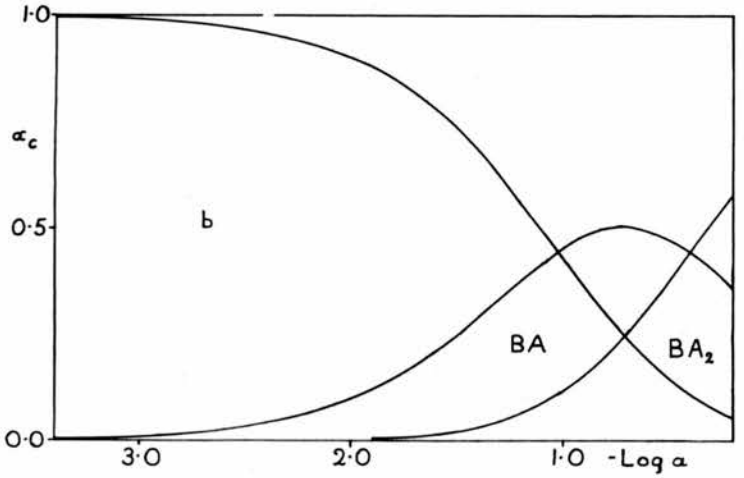
FIG. 5-10 Relative proportions of the species BA_n present in solution



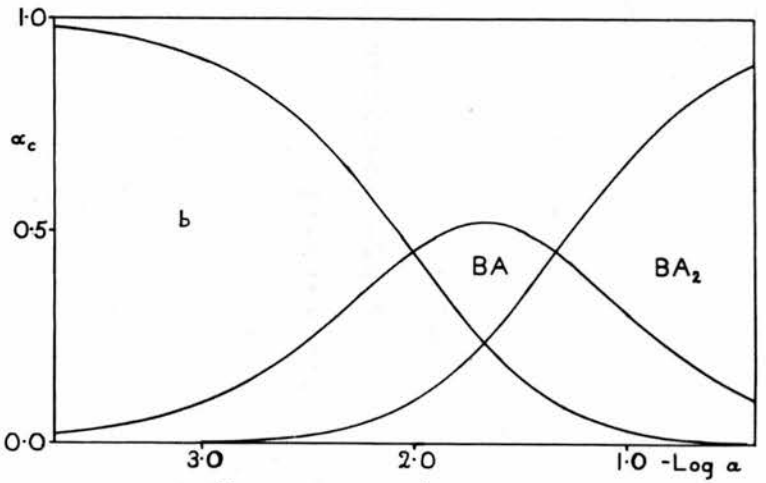
(a) Copper(II) cyanoacetate



(b) Copper(II) glycollate



(c) Copper(II) chloroacetate



(d) Copper(II) methoxyacetate

5 - B. DISCUSSION

The proportions, α_c, of the various species present in solution have been plotted as functions of log a in Figs. 5-10a - 5-10d for the cyanoacetate, chloroacetate, glycollate, and methoxyacetate systems respectively. Similar plots for the other three systems have not been given as the measurements do not reach very high values of $\bar{n}$, and the figures obtained would have resembled the left hand portions of those given.

As in the proton-carboxylate systems, the values of the free ligand concentration at the several points where the percentages of two species are the same, are related to the values of the stability constants. This is most completely illustrated in Fig. 5-12 which gives the proportions of the species present in the copper(II) glycollate system. The relationships between these "equality" points and the various constants are set out in Table 5-10.

The stability constants obtained for the copper(II) carboxylate complexes in this work, by Martin (1961), and Clarke (1960) are summarised in Table 5-11. No dimeric species have been detected in any of the systems herein, but the dimer Cu_2A_4 was identified in copper(II) propionate solutions. It is possible that the dimers represent only a small amount ($< 5\%$) of the total complexes present in solution. This may account for the apparent absence of dimers in other systems, in which they occur in the solid state and in organic solvents. [cf. Sec. 1 - D].

Table 5-10.

Relationships between values of log a and stability constants for copper(II) glycollate at points where percentages of two species are equal.

c equal for	log a	relationship i.e log a =
b, BA	2.50	$\log K_1$
b, BA_2	2.01	$\frac{1}{2}\log \beta_2$
BA, BA_2	1.52	$\log K_2$
b, BA_3	1.42	$\frac{1}{3}\log \beta_3$
BA, BA_3	0.89	$\frac{1}{2}\log K_2K_3$

Table 5-11.

Stability Constants for Copper(II) Carboxylate Complexes in 3.00M Sodium Perchlorate at 25.00 ± 0.05°C.

Ligand	log K_1	log K_2	log K_3	log β_2	log β_3
1. Formate*	1.53	0.89	0.26	2.42	2.68
2. Acetate*	1.79	1.15	-0.30	2.94	2.64
3. Propionate*	1.86	1.14		3.00	
4. Butyrate*	1.82	1.16		2.98	
5. Isobutyrate**	1.87	≤0.81		≤2.68	
6. Valerate**	1.92	≤1.10		≤3.02	
7. Trimethylacetate**	2.03	≤1.65		≤3.68	
8. Cyanoacetate	0.87	0.13		1.00	
9. Chloroacetate	1.02_5	0.40_5		1.43	
10. Glycollate	2.50	1.52	0.25	4.02	4.27
11. Methoxyacetate	2.01	1.33		3.34	
12. Phenoxyacetate	1.41	0.57		1.98	
13. Mandelate	2.38	1.58		3.96	
14. Phenylacetate	1.61	≤0.8		≤2.4	

* Martin ** Clarke

Such an amount would not be detectable by the present method but, as the dinuclear species has a much higher partition coefficient than the monomeric salt, it is identifiable by solvent extraction techniques (Graddon 1960; Rossotti et.al 1960). The occurrence of the dinuclear structure in crystalline copper(II) carboxylates is possibly caused by the dimer having a much lower solubility than the monomer and the former therefore is precipitated.

Sandell(1961) has investigated the equilibria present in the copper(II) methoxyacetate system in a 3.00M perchlorate medium, and claims to have identified the species BA, BA_2, BA_3, and BA_4. Examination of his formation curve shows that it is symmetrical about $\bar{n} = 1$, within the extent of the measurements. The projection strip prepared from the quoted data fitted the theoretical grid [Fig. 5-8] at all values of $\bar{n}$, indicating that the data can be interpreted by assuming only two complexes present. In the position of best fit $\log p^* = 0.43 \pm 0.01$ and $\log a_o = 1.40_5 \pm 0.01$ and by substitution in Eqs. (5-2) and (5-4)

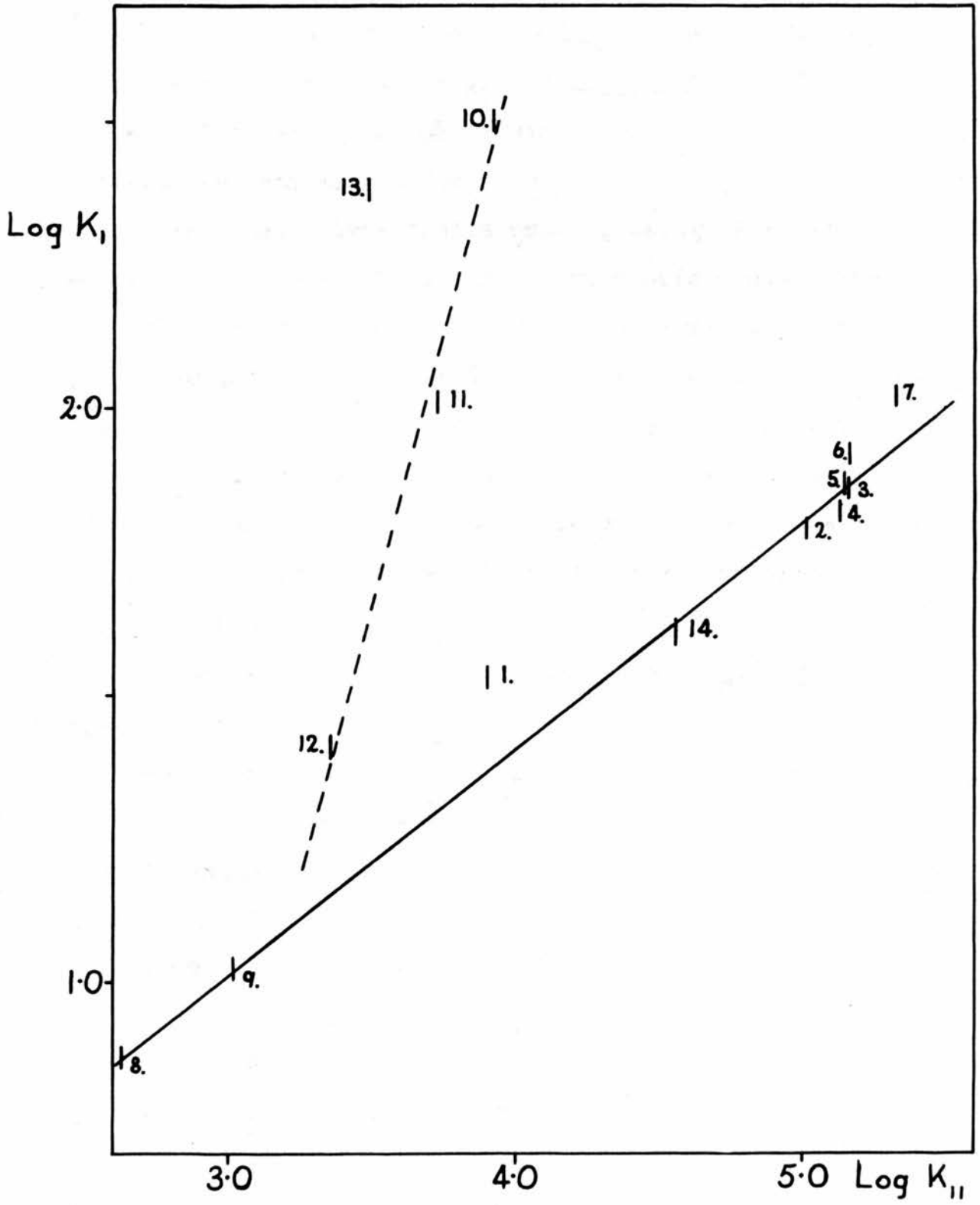
$$\log K_1 = 1.83_5 \pm 0.02$$

$$\log \beta_2 = 2.81 \pm 0.02$$

The values quoted are $\log K_1 = 1.79 \pm 0.02$ and $\log \beta_2 = 2.87 \pm 0.03$, but as the original interpretation contained four constants, some slight difference at least in the value of β_2 is not unexpected. Sandell's conclusions are apparently incorrect and, considering the very scanty data quoted, would appear to be unjustified.

It can be seen on examining Tables 4-9 and 5-11 that the strengths of the metal complexes are directly related to the strengths of the corresponding acids. This is most apparent when

FIG. 5-11 Log K_{11} as a function of log K_1 for the series of copper(II) carboxylate complexes. Numbers as in Table 5-11.



K_1 and K_{11} are compared. Although this parallelism had been observed in related work (Lloyd et.al.1951) there were some slight inconsistencies in the results. Similar relationships have been observed for other metal ions with series of closely related ligands, and have been reviewed by Rossotti(1960b).

A plot of log K_1 against log K_{11} is shown in Fig. 5-11. There is a fair linear relationship, shown by the full line, except for the formate, glycollate, methoxyacetate, mandelate, and phenoxyacetate systems. Some slight deviations from the linear relationship also occur in the valerate and trimethylacetate systems. This latter effect probably arises from the bulkier ligands causing an increase in the structure breaking effect of the complex on the solvent, and possibly shielding the coordinated metal ion from solvent contacts. Formic acid, the first member of the series, usually behaves anomalously, and, whereas all the rest can be regarded as substituted acetic acids, it cannot.

The enhanced stability of copper(II) glycollate, methoxyacetate, phenoxyacetate, and mandelate complexes may be ascribed to chelation through the oxygen atoms in the substituent groups to form five membered rings. The methoxyacetate and phenoxyacetate systems were studied to observe the effect of increasing the size of the groups attached to the oxygen atom through which chelation occurs. As the size of the group increases K_1 decreases more relative to K_{11} than found in the simple non-chelated systems, but the results show that some stabilisation by ring formation has occured. The more pronounced decreases in K_1 is considered to be caused by steric hindrance as the size of the

attached groups increases. There is, however, a parallelism between the stabilities of the proton and copper(II) carboxylates as shown by the broken line.

With the mandelate ion, on the other hand, chelation through the hydroxyl group is possible without any interference from the bulky phenyl group. This is supported by the high values obtained for the stability constants, similar to those for copper(II) glycollate. The slight decrease in K_1 compared with K_1 for copper (II) glycollate parallels the greater acidity of mandelic acid compared with glycollic acid. A tentative line through the mandelate and glycollate points appear to be approximately parallel to the major line but a number of related systems should be studied before conclusions can be reached.

Some supporting evidence for the chelation argument has been obtained from magnetic measurements on copper(II) glycollate, methoxyacetate, phenoxyacetate, mandelate, acetate and sulphate (Rossotti and Trotz 1961). If chelates are formed in the systems as suggested, then bridging by carboxyl groups will not be possible in the solid if this also crystallises as monomeric chelates, and a normal magnetic moment, corresponding to one unpaired electron, should be observed. This was in fact found. Copper(II) acetate had a magnetic moment of 1.4_5 B.M. indicating the dinuclear structure, whereas the other carboxylates had moments of 1.9 B.M., very similar to the value of 1.9_4 B.M. found for copper (II) sulphate.

The conclusion that copper(II) phenoxyacetate has a chelated structure is contrary to the suggestion of Perrin(1961). He

compares K_1 for some substited copper(II) phenoxyacetates with K_1 for copper(II) acetate and chloroacetate and concludes that the former are not chelates. Although copper(II) phenoxyacetate is less stable than copper(II) acetate, it is twice as stable as would be expected simply from K_{11} for phenoxyacetic acid. The large phenyl group puts strain on the chelate ring by being in close proximity to the copper(II) ion. The magnetic results give some support to the inferences drawn from the values of the stability constants.

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